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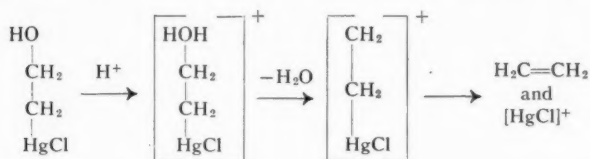
REVERSIBILITY OF ALKENE OXYMERCURATION¹

A. RODGMAN, D. A. SHEARER, AND GEORGE F WRIGHT

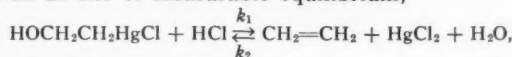
ABSTRACT

It has been shown that deoxymercuration (conversion of an α -oxyorganomercurial to the alkene) is a second-order reaction dependent on concentration of the mercurial and of the deoxymercuring acid. Moreover the rate of deoxymercuration increases with basic strength of the alkoxy substituent in the mercurial. This tendency would indicate that the rate was dependent on the strength of the acid used for deoxymercuration. The supposition has been proved by use of trifluoroacetic acid which decomposes α -2-methoxycyclohexylmercuric trifluoroacetate more slowly than does hydrochloric acid. The trifluoroacetoxymercurial decomposes to the extent of 35% whereas its synthesis is effected in 60% maximum yield from cyclohexene and mercuric trifluoroacetate. A measurable equilibrium is thus attained in this oxymercuration, though not necessarily because of a simple reversible reaction.

Whitmore has suggested that the conversion of alkaneoxymercurials to alkenes is dependent on the hydrogen ion concentration of the system (14). In terms of the decomposition of β -hydroxyethylmercuric chloride this may be expressed as follows:



This opinion is at variance with that of Sand and Breest (11), who effected a conductimetric study in which this oxymercurial was treated with hydrochloric acid. They described the reaction as one of measurable equilibrium,



from which the constant may be derived:

$$K = k_1/k_2 = [\text{H}^+][\text{Cl}^-][\text{HOCH}_2\text{CH}_2\text{HgCl}]/[\text{HgCl}_2][\text{CH}_2=\text{CH}_2]$$

where $k_1 = 1.21 - 1.34 \times 10^{-7}/p$ and $k_2 = 2.81 \times 10^{-7}/p$. In these constants p is the solubility of ethylene in the system at 1 mm. pressure.

This expression may be questioned from several aspects. First it implies a measurable equilibrium which has not been observed in unbuffered systems of alkenes and mercuric chloride. Secondly the participation of trichloromercurate and tetrachloromercurate ions is not so significant as Sand and Breest thought them to be (6). Actually the experimental method is not sufficiently definitive in consideration of the conclusions which were drawn (1).

¹Manuscript received July 18, 1957.

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

In order to test the rate dependence specified by Sand and Breest we have examined the system of alkoxycyclohexylmercuric halides in methanolic hydrogen chloride using the colorimetric analysis for inorganic mercury which has been described previously (2). First we have examined the reaction of mercuric chloride with cyclohexene in anhydrous methanol and find (Fig. 1) that even if the slight diminution in mercuric chloride

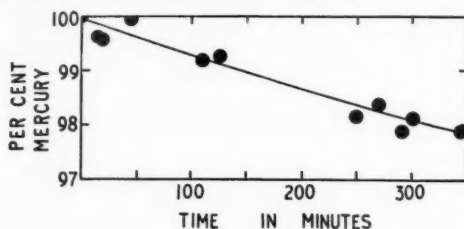


FIG. 1.

could be attributed to the reaction of oxymercuration it would be so slow and so slight that it might be ignored during kinetic treatment of the deoxymercuration. Secondly we have decomposed near-anhydrous methanolic solutions of α -2-methoxycyclohexylmercuric chloride (1.0×10^{-3} mole/liter) by treatment with hydrogen chloride and find the reaction to be first order in respect of oxymercurial and first order in respect of the acid. Thus at an acid concentration of 0.5×10^{-3} mole/liter (80% of reaction) the rate constant is $0.65 \text{ liter mole}^{-1} \text{ sec}^{-1}$. At 1.0×10^{-3} mole/liter of acid (75% investigated) the constant is $0.64 \text{ liter mole}^{-1} \text{ sec}^{-1}$ while at 2.0×10^{-3} mole/liter of hydrogen chloride (90% investigated) the constant is $0.63 \text{ liter mole}^{-1} \text{ sec}^{-1}$. Moreover it may be seen in Table I that the second-order decomposition is unaffected by inclusion either of sodium chloride or of mercuric chloride. Therefore the decomposition of this oxymercurial seems not to be dependent on the anion, either as chloride ion or as tetrachloromercurate ion.

TABLE I

DECOMPOSITION OF α -2-METHOXYCYCLOHEXYLMERCURIC CHLORIDE BY HYDROGEN CHLORIDE (BOTH 1.0×10^{-3} MOLE/LITER) IN ANHYDROUS METHANOL AT 25° WITH ADDED SODIUM CHLORIDE AND MERCURIC CHLORIDE

Reagent added		% Reaction investigated	k , liter mole ⁻¹ sec. ⁻¹
Reagent	Mole/liter		
None	—	—	0.64
NaCl	1.0×10^{-3}	72	0.64
NaCl	2.0×10^{-3}	70	0.65
NaCl	3.0×10^{-3}	75	0.66
HgCl ₂	1.0×10^{-3}	72	0.63
HgCl ₂	2.0×10^{-3}	70	0.64
HgCl ₂	3.0×10^{-3}	70	0.66

This result does not support the opinion of Chatt (5), who disagrees with Whitmore's implication that deoxymercuration is dependent on acid strength. Chatt claims that nitric and sulphuric acids do not decompose halogen-free mercurials but this statement is not in accord with fact. For example α -2-methoxycyclohexylmercuric acetate is converted to cyclohexene either by cold nitric or by hot acetic acid (3). However, more definitive evidence is provided by the dependence of deoxymercuration rate upon the basicity of the ether function in the oxymercurial.

This dependence of deoxymercuration rate upon the electron-donating propensity of the ether function is shown in Fig. 2 and listed in Table II. This series of α -2-oxycyclohexyl-

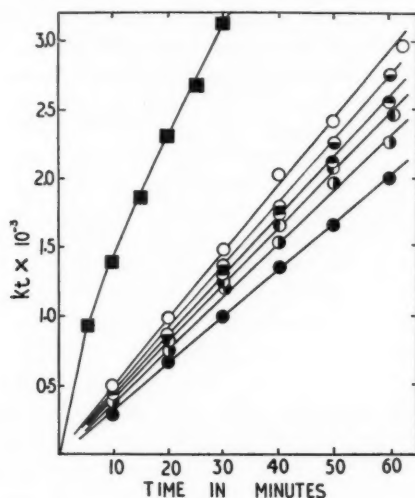


FIG. 2.

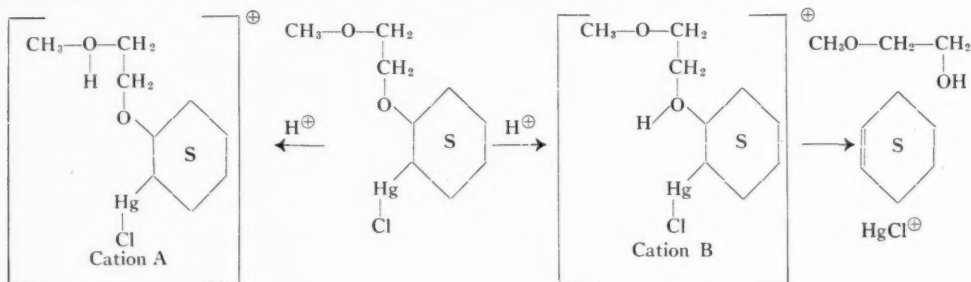
mercuric halides has been treated with hydrogen chloride in near-anhydrous methanol, and then the systems have been analyzed by the colorimetric analytical method (6). This method probably gives high results for the most rapid of these reactions (the deoxymercuration of 2-hydroxycyclohexylmercuric chloride) because of incomplete extraction by chloroform of the hydroxyorganomercurial. This analytical failure, shown in Fig. 2 as a variation in slope of the second-order rate with respect to time, serves in a sense to support the reliability of the other slopes of Fig. 2 and the recorded rate constants of Table II.

TABLE II
DECOMPOSITION OF α -2-ALKOXYCYCLOHEXYLMERCURIC CHLORIDE,
 $\text{ROC}_6\text{H}_{10}\text{HgCl}$ (1.0×10^{-1} MOLE/LITER), BY HYDROGEN CHLORIDE IN
METHANOL AT 25°C .

Symbol, Fig. 2	R	HCl, mole/liter $\times 10^{-3}$	k_t , liter mole $^{-1}$ sec. $^{-1}$
●	$\text{CH}_3\text{O}-\text{C}_2\text{H}_4-$	0.5	0.56
●	$\text{CH}_3\text{O}-\text{C}_2\text{H}_4-$	1.0	0.56
●	$\text{CH}_3\text{O}-\text{C}_2\text{H}_4-$	2.0	0.54
◐	Me	1.0	0.64
◐	Et	1.0	0.68
◐	Pr	1.0	0.71
◐	iso-Pr	1.0	0.75
◐	<i>t</i> -Bu	1.0	0.81
■	H	1.0	ca. 1.0

The monoethers of Table II are arranged in order of increasing rate constant for the deoxymercuration reaction. But this is the same order of basicity (co-ordinative electron donation) which is characteristic of the parent alcohols corresponding to these alkoxy

substituents. In view of this correlation the methoxyethyl analogue (top, Table II) might seem to behave anomalously in its slow deoxymercuration because such vicinal polyethers are known to be strongly co-ordinative. One must presume in this instance that co-ordination of the deoxymercurating agent with the ultimate ether-oxygen (Cation A) is ineffective toward the scission from which the alkene is formed. This diversion of co-ordination may be expressed in Whitmore's terms:



It must be assumed in this formulation of reaction that decomposition of the effective ion (Cation B) is very fast and that the rate is that of co-ordination of hydrogen ion with the oxymercurial. It is obvious that this description of the second-order rate does not depend upon ionic species but could as well involve co-ordination of molecular acid with an oxymercurial. The likelihood of a molecular reaction will be discussed in a forthcoming publication. In the present report the ionic mechanism will be considered in relationship to the acid strength of the decomposing reagent.

Unfortunately there is still insufficient knowledge of acid dissociations in non-aqueous media. However, one may assume that trifluoroacetic acid, which seems to have an acid strength comparable with hydrochloric acid in water, will be about half as strong in near-anhydrous methanol. This assumption is made by reference to the evaluation of acid strength of trifluoroacetic acid in 70% acetone-water (8).

Deoxymercuration occurs when α -2-methoxycyclohexylmercuric trifluoroacetate is prepared from the analogous chloromercurial by treatment with silver trifluoroacetate and then is treated in methanol with trifluoroacetic acid. Kinetic analyses of this reaction, recorded in Table III, show that the initial rate is much slower (compare with Table II) than that observed when the chloromercurial is deoxymercurated by use of hydrogen chloride. Therefore it would appear that the strength of the acid is significant to the rate of deoxymercuration.

TABLE III
DECOMPOSITION OF α -2-METHOXYCYCLOHEXYLMERCURIC TRIFLUOROACETATE BY TRIFLUOROACETIC ACID (BOTH 4×10^{-3} MOLE/LITER) IN METHANOL AT 25° C.

Time, min.	$C_9H_{13}F_3HgO_3$, mole/liter	k , liter mole ⁻¹ sec. ⁻¹
0	4.00	—
10	3.68	0.037
20	3.44	0.034
30	3.23	0.033
60	3.08	0.021
90	2.80	0.019
120	2.56	0.012
150	2.62	0.0125

It may be seen in Table III that the rate constant calculated for a unidirectional second-order reaction decays rapidly with respect to time. Indeed the constancy of organomercurial after 120 minutes indicates that an equilibrium has been reached after 35% has been consumed. Confirmation of this equilibrium state is established by treatment of cyclohexene in methanol with mercuric trifluoroacetate. The exact amount of α -2-methoxycyclohexylmercuric trifluoroacetate that is produced in this manner has been found by treatment of the system with aqueous sodium chloride. The chloromercurial isolated in this manner does not exceed a 60 mole per cent yield.

The demonstration of this equilibrium specifies the reaction of mercuric trifluoroacetate with cyclohexene in methanol as intermediate between the virtual non-reactivity of mercuric chloride and the essentially quantitative conversion by methanolic mercuric acetate. These differences conform with the probable differences in acid strength.

It would be easy to conclude from these results that the equilibrium demonstrated for the cyclohexene-mercuric trifluoroacetate-methanol system (and by analogy for all oxymercuration) was the result of a simple reaction like Whitmore's deoxymercuration of β -hydroxyethylmercuric salt in which complete reversibility existed. This conclusion would not be supported by experiment. For example boron fluoride catalyzes oxymercuration but not deoxymercuration (12). Also the oxymercuration now known seem not to be acid catalyzed (9) as we have found deoxymercuration of α -2-methoxycyclohexanemercuric salts to be. In brief these examples show that oxymercuration must be more complex than can be explained as a reversal of Whitmore's deoxymercuration mechanisms.

EXPERIMENTAL*

α -2-Isopropoxycyclohexylmercuric Chloride

To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 30 ml. of propanol-2 was added 0.90 g. (0.011 mole) of cyclohexene. After 3 hours, filtration into 25 ml. of 5% aqueous sodium chloride at 0° C. precipitated 3.05 g. (80%) of the isopropoxymmercurial, m.p. 90.5–91.5° C. Crystallization from absolute ethanol (20 ml./g.) raised the melting point to 94.8–95.5° C. Calc. for $C_9H_{17}ClHgO$: C, 28.7; H, 4.52; Hg, 53.2. Found: C, 28.4; H, 4.68; Hg, 52.2.

α -2-Alkoxycyclohexylmercuric Halides Used in Kinetic Studies

These oxymercurationals, prepared by standard procedures, were purified to melt as shown in Table IV.

TABLE IV
MELTING POINTS OF 2-ALKOXYCYCLOHEXYLMERCURIC HALIDES,
 $ROC_6H_{10}HgX$

Diastereomer	R	X	M.p., ° C.	Reference
α	Me	Cl	115.2–116.0	(17)
β	Me	Cl	114.1–114.5	(10)
α	Et	Cl	60.8–61.5	(3)
α	Pr	Cl	57.5–58.5	(9)
α	<i>t</i> -Bu	Cl	115.0–116.0	(3)
α	MeOC ₂ H ₄	Cl	121.5–122.5	(9)
α	H	Cl	153.0–153.6	(3)
α	Me	Br	114.0–114.5	(10)
α	Me	I	81.4–82.0	(4)

*Melting points have been corrected against reliable standards (16). X-Ray diffraction data have been obtained with $Cu K_{\alpha}$ (Ni filtered) radiation at d spacings in Å at visual relative intensities I/I_1 .

Preparation of Mercuric Trifluoroacetate

Mercuric trifluoroacetate was prepared by solution of 10.83 g. (0.05 mole) of mercuric oxide in 10 ml. (0.147 mole) of trifluoroacetic acid. After the initial evolution of heat a further 5-ml. portion of trifluoroacetic acid was added, and the whole was heated on the steam bath until solution was almost complete. The hot suspension was filtered through sintered glass and chilled to 0° C. The white crystals were filtered off and vacuum dried, 10.9 g. (53%), m.p. 164–168° C. with softening at 158° C. The X-ray diffraction pattern was: [20] 10.00; [18] 10.64; [16] 15.49, 13.71; [14] 4.90; [12] 7.82, 4.18; [10] 4.07, 3.40, 3.15; [8] 4.48, 3.53; [6] 5.27, 3.91, 2.98, 2.66, 2.28; [4] 6.91, 3.76, 2.93, 2.36, 2.23, 2.03; [2] 6.44, 5.49, 4.76, 3.33, 2.77, 2.00, 1.96, 1.93; [1] 7.49, 5.71, 2.59, 2.48. Calc. for $\text{Hg}(\text{CF}_3\text{COO})_2$: Hg, 47.0. Found: Hg, 46.8, 46.7.

Trifluoroacetoxymercuration of Cyclohexene

A solution of 1.07 g. (0.0025 mole) of mercuric trifluoroacetate in 10 ml. of pure methanol was let stand 1 hour, then 0.25 ml. (0.0025 mole) of pure cyclohexene was added. Reaction was terminated by dilution into aqueous sodium chloride. The yield of α -2-methoxycyclohexylmercuric chloride was determined by solution of the precipitate in chloroform and evaporation of this solution under reduced pressure. After a 3-minute reaction time the product weighed 0.38 g. (44%) while a 60-minute reaction time increased this yield to 58%. In both instances the product melted at 114–115° C.; a mixture melting point was not lowered. The yield was not appreciably increased by longer reaction time.

 α -2-Methoxycyclohexylmercuric Trifluoroacetate

To a solution of 2.21 g. (0.01 mole) of silver trifluoroacetate (X-ray diffraction: [20] 3.62; [18] 6.41, 6.06; [12] 2.56, 2.32; [10] 3.01, 2.69; [8] 3.32, 2.29; [6] 2.60, 2.51, 2.41; [2] 3.50, 3.15, 2.15; [1] 2.10) in 25 ml. of distilled water was added 3.40 g. (0.0097 mole) of α -2-methoxycyclohexylmercuric chloride; the resulting suspension was agitated at 20° C. for an hour. The precipitated silver chloride was removed by filtration, and washed with water, ethanol, and ether. It weighed 1.43 g. (101%).

The combined filtrates were distilled under reduced pressure, leaving a gummy solid (4.17 g., 97%, m.p. 63–75° C.). This gum was dissolved in warm ethanol (60° C., 2.5 ml./g.) containing 0.3 g. of Norit, then filtered. The filtrate, diluted with 35 ml. of petroleum ether (b.p. 60–70° C.), gave a granular solid upon seeding, wt. 2.58 g., m.p. 73.8–74.8° C. Recrystallization from hot ethanol–petroleum ether (1:9) without seeding gave 1.55 g., m.p. 128–129° C. Solution of 0.1 g. of this compound, m.p. 128° C., in ethanol, followed by dilution with the same petroleum ether (b.p. 60–70° C.) and with addition of the seeds, m.p. 73° C., gave 0.08 g., m.p. 73.8–74.5° C. Calc. for $\text{C}_9\text{H}_{13}\text{F}_3\text{O}_3\text{Hg}$: Hg, 47.1. Found: Hg, 47.6. Treatment of 0.42 g. (0.001 mole) of this mercurial in ethanolic solution with aqueous sodium chloride gave 0.30 g. (85%) of α -2-methoxycyclohexylmercuric chloride, m.p. 114.2–115.0° C.

Kinetic measurements were made at $25.0^\circ \pm 0.1^\circ \text{C}$. The methanol was purified under nitrogen by Lund and Bjerrum's method (7) and was free from peroxide (TiCl_3 test) and aldehyde (Schiff test). Solutions of hydrogen chloride in methanol were prepared from hydrogen chloride which had been dried by passage through sulphuric acid. The trifluoroacetic acid was purified by distillation while the diphenylthiocarbazon (dithi-zone) was prepared by the method of Winkler (15, 13). The kinetic procedure and apparatus was essentially that reported previously (2, 9).

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ADDITION OF *n*-BUTYL MERCAPTAN TO 1-PENTENE ON IRRADIATION WITH X-RAYS OR GAMMA RAYS

I. 140 KVP. X-RAYS¹

A. FONTIJN² AND J. W. T. SPINKS

ABSTRACT

n-Butyl mercaptan reacts with 1-pentene when irradiated with X-rays. The dependence of reaction rate upon concentration of mercaptan and pentene has been studied as well as the dependence on dose rate. A comparison with the photoinitiated reaction is made.

INTRODUCTION

Radiation Chemistry

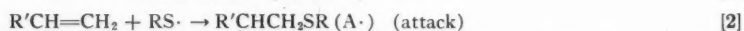
Radiation chemistry deals with the chemical effects of all ionizing radiations. It includes the effects of high energy radiations such as X and γ rays and of high energy particles such as α and β rays. In passing through matter these radiations lose their energy, producing excited molecules and ions. Free radicals are often formed which may combine with each other or with other reacting species.

Reactions have been studied in the gas, liquid, and solid phase, and it was the aim in the present work to study a liquid phase reaction, namely that between 1-pentene and *n*-butyl mercaptan, and to make a comparison with the photoinitiated reaction.

Addition Reactions of Mercaptans to Olefins

Free radical chain addition reactions of mercaptans to olefins, yielding products of anti-Markownikow configuration, have been reported by Kharasch and co-workers (12, 13, 14).

Chain reactions of this kind are thought to involve three essential steps. The first step involves the generation of mercaptyl ($\text{RS}\cdot$) radicals. The second step consists in the additive reaction of a mercaptyl free radical with an olefin molecule, forming another free radical. The third step completes the reaction through interaction of the free radical formed in the second step with a molecule of mercaptan, at the same time regenerating the chain initiating mercaptyl free radical.



Oxidants were used as chain initiators by Kharasch and co-workers, but they did not report the reaction between *n*-butyl mercaptan and 1-pentene. Oxygen itself acted as a chain inhibitor.

Kharasch, Nudenberg, and Meltzer (15) reported the addition of mercaptan to styrene, initiated by the photolytic dissociation of organic disulphides into mercaptyl radicals.

The photoinitiated addition of *n*-butyl mercaptan to 1-pentene was studied by Back, Trick, McDonald, and Sivertz (2). The initiation was either by direct photolysis of mercaptan or by the use of AIN (2,2'-azo-bis-isobutyronitrile; $\text{C}(\text{CH}_3)_2(\text{CN})-\text{N}=\text{N}-\text{C}(\text{CH}_3)_2(\text{CN})$). These reactions were carried out in benzene solution at 25°C.

¹Manuscript received July 2, 1957.

Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan.

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The mechanism of these reactions is again described by reactions [1-3]. It was suggested that the kinetic chain could be broken by the following reactions:



At lower rates of initiation, chain lengths of over 10^4 were observed.

The reaction rate was reported to be proportional to the square root of the intensity, thus allowing the evaluation of the average lifetime of the free radical chains and the rate constants by using the rotating sector method of intermittent illumination (2, 20). This latter method has been used for a number of photochemical and radiation chemical chain reactions (9, 10, 18). The average lifetime of the free radical chains for a solution, 1 molar in each of butyl mercaptan and 1-pentene, was found to be 0.0074 seconds for an initiation rate of 1.3×10^{-6} M./l./sec.

To get an estimate of the role of oxygen, Back, Trick, McDonald, and Sivertz (2) did experiments with both systems which had not been degassed and systems degassed under high vacuum by alternate freezing and melting. In the latter case the reaction rate was nearly twice as great, and the inhibition periods were greatly reduced, but never completely eliminated for the 1-pentene, *n*-butyl mercaptan system. Oxygen is known (7, 3) to react readily with most free radicals forming a peroxide radical:



Reactions of this kind will inhibit the chain reaction until most of the oxygen is used up.

It was the aim of the present work to see whether the reaction between 1-pentene and *n*-butyl mercaptan would also occur under the influence of ionizing radiation, and, if so, to compare the kinetics with those for the photoinitiated reaction.

In order to make a close comparison with the photoinitiated reaction, the procedures of Sivertz *et al.* were followed as closely as possible. However, benzene was used as solvent in only a few experiments and cyclohexane in the majority of experiments, since benzene often exhibits a protective effect against ionizing radiations (17).

The reactions were carried out in a dilatometer and the rate was determined by observing the drop of the meniscus in the capillary of the dilatometer. This contraction was then related to the mercaptan disappearance by an amperometric titration of the residual mercaptan.

EXPERIMENTAL METHODS

A. Chemicals

Phillips research grade 1-pentene (mole per cent purity 99.5), Nichols reagent thiophene-free benzene, and Fisher reagent cyclohexane were used without further purification (2).

n-Butyl mercaptan was obtained from Matheson, Coleman, and Bell Incorporated. It was purified following a procedure suggested to us by Dr. C. Sivertz. The mercaptan was dissolved in a 20% NaOH solution, forming the water-soluble sodium salt, $\text{C}_4\text{H}_9\text{SNa}$. The impurities were then extracted by shaking three or four times with ether. A 20% H_2SO_4 solution was then added to regenerate the mercaptan, which formed a separate liquid layer. The two layers were then separated. The mercaptan was washed several times with distilled water, then dried over anhydron. Distillation through a short Vigreux column followed. The fraction boiling at 96–97° C. at 715 mm. was used.

B. Radiation Source

X-Rays were obtained from a 140 kvp. X-ray machine (General Electric KX-10), operated at 5 ma., and filtered through 1 mm. of Al. The filtered beam had a half value layer of 3.25 mm. Al and the output of the machine was constant within 3-5%.

C. Dilatometers

The reactions were carried out in pyrex glass dilatometers. Each consisted of a bulb made from an ordinary 18×150 mm. test tube sealed to a capillary tube (20 cm. long, 10 mm. outside diameter). The capillary tube ended in a short piece of 8 mm. glass tubing having a constriction to allow the dilatometer to be sealed off under vacuum at that point. On the other end of this tube was a 10/30 ground glass joint.

The inside diameters of the capillary tubes were determined, and the cross sections calculated. The average value was 0.0630 cm.². The cross sections for some dilatometers differed from the average by about 5% and, in these cases, a suitable correction was applied to the measured meniscus movements.

The average value of the total volume of the bulb and capillary was 18.7 cm.³ and all but two of the dilatometers had volumes within 2% of this value. The two exceptions had volumes 4.5% and 6.4% higher than the average and the reported meniscus drop rates for these dilatometers are the observed ones decreased by 4.5% and 6.4% respectively. Such a volume correction is based on the assumption that the contraction in units of volume is proportional to the volume irradiated. This would only be an exact procedure for a completely uniform irradiation intensity over the whole volume of the dilatometer bulb. This is however probably not the case since geometrical factors, back-scatter from the water in the water bath, and absorption in the dilatometer bulb, will play a role. For this reason no volume corrections are made for the other dilatometers used.

D. Preparation of the Reaction Mixture

Since one of the aims was to make a comparison with the photoinitiated reaction, the methods of Sivertz were followed as closely as possible (2).

The reaction mixture was prepared in volumetric flasks and was poured into the dilatometer through a capillary funnel. No contraction, upon mixing the reagents, was observed. All glassware used was cleaned with chromic acid cleaning solution, then washed several times with distilled water, and finally with Merck reagent acetone. The dilatometers were dried by evacuation, the volumetric flasks and pipettes with compressed air. After filling, the dilatometer was attached to a vacuum line and the greater part of the dissolved air removed by alternate freezing and melting. The dilatometer was finally sealed off while the mixture was frozen and under vacuum. Although this "alternate freezing and melting" technique removed a good deal of the dissolved air, it probably did not get rid of all of it (some bubbles could still be observed at the final melting). The vacuum was 1.5×10^{-2} mm. Hg or better.

E. The Irradiations

The irradiations were carried out in a constant temperature water bath fitted with a $\frac{1}{16}$ inch lucite window and kept at $30 \pm 0.03^\circ$ C. The dilatometer bulb was placed about $\frac{1}{2}$ cm. behind the window. In this way there was only a slight attenuation of the radiation in its path to the reaction mixture. The material surrounding the reaction mixture was thick enough to obtain electronic equilibrium.

The intensity of the radiation received by the reaction mixture could be changed by varying the distance between the radiation source and the water bath.

The drop of the liquid meniscus in the dilatometer capillary was followed using a cathetometer reading to ± 0.005 cm.

F. Dosimetry

The energy absorbed by the reaction mixture was determined by ferrous sulphate dosimetry (21). Test tubes of the same size and material as the dilatometer bulbs were used, clamped in the water bath in exactly the same position as the dilatometers. They were filled with an aerated solution of ferrous ammonium sulphate in $0.8 N H_2SO_4$, over a length corresponding to the length of a dilatometer bulb. The test tube was only half full and sufficient contact with the atmosphere existed that there was no danger of depletion of oxygen in the dosimeter solution.

EXPERIMENTAL RESULTS

A. Observations

1. Reaction Rates

The reaction mixture contracts upon irradiation, producing a drop of the meniscus of the liquid in the capillary of the dilatometer. The results obtained are summarized in Table I. The reaction rate given in this table is obtained from the linear part of the graph of centimeters' drop versus minutes' irradiation. A few typical curves are given in Fig. 1.

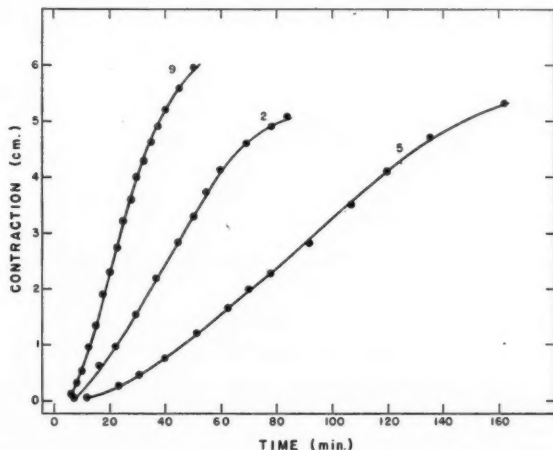


FIG. 1. Dilatometric measurement of the rate of addition of *n*-butyl mercaptan to 1-pentene; typical curves. The numbers indicate the number of the experiment.

These curves show a short inhibition period followed by a slight curve, then a straight part, and then, if the irradiation is continued long enough, a levelling off. The inhibition periods, given in Table I, indicate the number of minutes after the start of the irradiation during which no movement of the meniscus could be observed.

Experiment 1 was made with a reaction mixture which had not been degassed. In all the other experiments the reaction mixtures were degassed by alternate freezing and melting. In experiments 1-7 the concentrations used were 0.96 M./l. *n*-butyl mercaptan and 0.95 M./l. 1-pentene, in cyclohexane solution. Experiments 2, 3, and 4 were all done at the same dose rate. Experiment 3 was only irradiated for a short time to obtain

TABLE I

SUMMARY OF REACTION RATES FOR IRRADIATION OF MIXTURES OF BUTYL MERCAPTAN AND PENTENE IN CYCLOHEXANE SOLUTION AT 30° C. USING 140 KVP. X-RAYS

Experiment No.	Concentration		Rate of energy absorption, ergs/g./min. $\times 10^{-3}$		Reaction rate, cm./min.	Inhibition period, minutes
	M./l. C_4H_9SH	M./l. C_5H_{10}	Measured ^a	Corrected ^b		
1 ^c	0.96	0.95	35	25	0.031	120
2	0.96	0.95	35	25	0.091	6
3	0.96	0.95	35	25	—	5
4	0.96	0.95	35	25	0.088	6
5	0.96	0.95	18	13	0.044	11
6	0.96	0.95	12	9	0.026	9
7	0.96	0.95	6	4	0.015	21
8	0.96	4.44	35	26	0.131	6
9	0.96	3.12	35	26	0.174	5
10	0.96	1.87	35	25	0.134	6
11	0.96	1.43	35	25	0.104	5
12	0.96	1.43	35	25	0.126	4
13	0.96	0.475	35	25	0.034	5
14	0.96	—	35	25	0.000	—
15	1.91	0.95	35	34	0.080	5
16	1.44	0.95	35	30	0.067	6
17	0.48	0.95	35	21	0.058	4
18	0.29	0.95	35	19	0.026	9
19	—	0.95	35	17	0.000	—
20	1.86	2.17	35	33	0.263	2
21 ^d	4.5	4.7	35	60	0.790	—
22 ^d	4.5	4.7	18	31	0.350	—
23 ^d	4.5	4.7	12	21	0.260	—
24 ^d	4.5	4.7	6	10	0.081	4
25 ^e	0.97	0.95	35	26	0.029	20
26 ^e	0.97	0.95	35	26	0.027	11

^aAbsorptions as measured with a Fricke dosimeter.^bThese doses corrected for the difference in effective atomic number between the reaction mixture and 0.8 N H_2SO_4 .^cNot degassed.^dNo solvent.^eBenzene as solvent, instead of cyclohexane.

a value for the graph of centimeters' drop versus mercaptan disappeared (Fig. 5). Experiments 5-7 were carried out at a different dose rate. In this way data for a plot of the reaction rate versus intensity were obtained (Fig. 2).

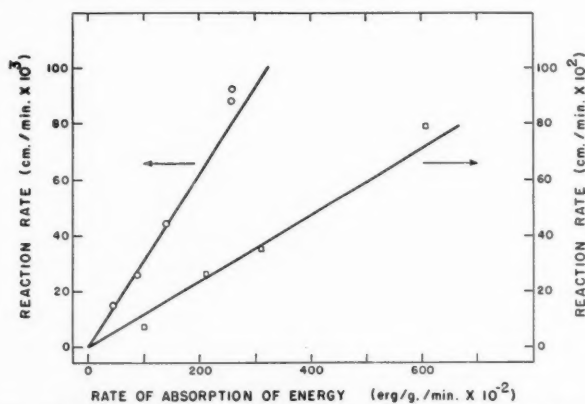


FIG. 2. Reaction rate as a function of the rate of absorption of energy. ○, butyl mercaptan, 0.96 M./l., pentene, 0.95 M./l.; □, butyl mercaptan, 4.5 M./l., pentene 4.7 M./l.

In experiments 8-14 the 1-pentene concentration was varied, the *n*-butyl mercaptan concentration being kept constant. In experiments 15-19 the *n*-butyl mercaptan concentration was varied, the pentene concentration being kept constant. In this way, Figs. 3 and 4, giving the dependence of the reaction rate on the concentration, were obtained. In experiment 20 both the 1-pentene and *n*-butyl mercaptan concentrations were higher than in experiments 1-7.

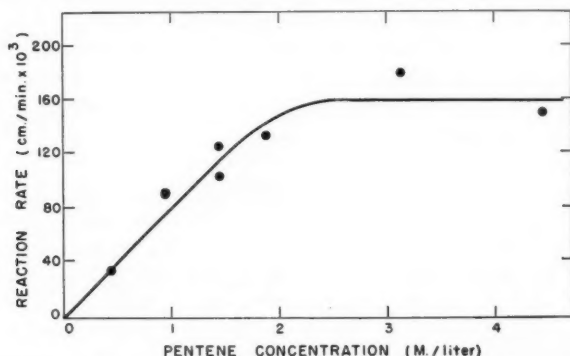


FIG. 3. Reaction rate as a function of the 1-pentene concentration at constant butyl mercaptan concentration (0.96 M./l.) in cyclohexane solution. Rate of absorption of energy, 19000 ergs/cc./min.

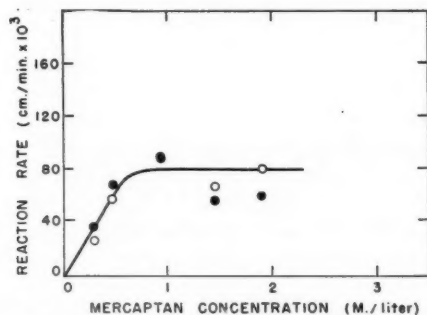


FIG. 4. Reaction rate as a function of the *n*-butyl mercaptan concentration at constant 1-pentene concentration (0.95 M./l.) in cyclohexane solution. O, observed values; ●, values corrected for a standardized dose rate of 19000 ergs/cc./min.

Experiments 21-24 were carried out using equimolar quantities of *n*-butyl mercaptan and 1-pentene, in the absence of solvent. The results obtained are also plotted in Fig. 2.

In experiments 25 and 26 benzene was used as solvent instead of cyclohexane. This was done to see whether any radiation protection by benzene as compared to cyclohexane existed in this system (17).

2. Inhibition Period

The mixture in experiment 1 was not degassed and the inhibition period lasted 2 hours. In experiments 2, 3, and 4, which were done under similar conditions to 1, but where the mixture was degassed by alternate freezing and melting, the inhibition period was reduced to 5 or 6 minutes. The rate in experiment 1 was considerably lower than in experiments 2 and 4.

From Table I it appears that the inhibition periods vary somewhat, but, in general, a lower rate corresponds to a longer inhibition period. In agreement with the results of other workers (2), the inhibition period is not completely reproducible. Lack of reproducibility may be partly due to inaccuracy in the observations, and partly to a variation of the small amount of oxygen which is still present after deaeration (5).

A further interesting observation as to the nature of these inhibition periods, still present after degassing, can be made from experiments 21 and 22. In these experiments, in which the reaction rate was considerably higher than in any of the other reactions, the liquid meniscus first rose before it dropped. This effect is similar to the Draper effect in photochemistry. The effect was the greater the faster the reaction. This effect could be responsible for part of the supposed inhibition periods, observed in the slower reactions even after degassing.

3. Levelling Off of Reaction Rate Curve

If the irradiation is continued for a sufficiently long period of time, the reaction rate curve eventually levels off. The reactant present at the lower molar concentration always governs the point at which the levelling off starts, and it can be shown that this is an indication that an equimolar (AB) or nearly equimolar addition product is being formed. (See below for an analysis of the product.)

4. Dark Reaction Rate

In various experiments in cyclohexane solution the liquid meniscus was observed during periods up to 60 minutes previous to the irradiation. No change was observed, and the dark reaction rate is therefore negligible compared to the radiator-induced reaction rate.

B. Analysis

1. Mercaptan Disappearance

The amount of butyl mercaptan present after irradiation, and hence, by difference, the butyl mercaptan disappearance, was determined by an amperometric titration with silver nitrate. The method followed was a slight modification of the one described by Kolthoff and Harris (16).

All determinations were carried out in duplicate. The accuracy is within 2%.

Fig. 5 gives a graph of centimeters' contraction versus mercaptan disappearance,

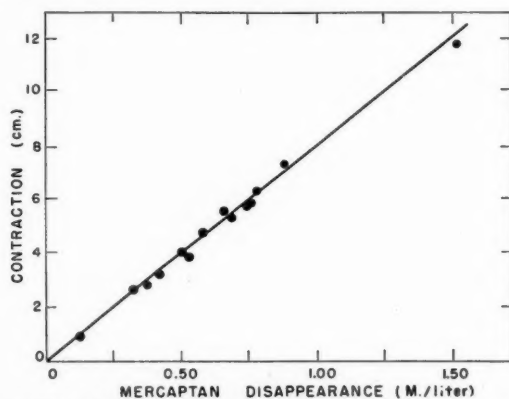


FIG. 5. Observed contraction in dilatometer as a function of the change in concentration of *n*-butyl mercaptan.

obtained in this way from a number of experiments. It shows a strict proportionality between observed contraction and mercaptan disappearance and this makes it possible to convert the reaction rate from cm. contraction/min. into M./l./min.

2. The Reaction Product

A reaction according to equations 1, 2, and 3 results in the formation of the ordinary anti-Markownikow product *n*-butyl *n*-amyl sulphide. A Markownikow addition reaction would result in the formation of *n*-butyl 2-amyl sulphide. Back (1) prepared both these products and the *n*-butyl 3-amyl sulphide from the corresponding amyl bromides. He also prepared the mercury chloride addition products following a procedure given by Faragher, Morrell, and Comay (6).

The *n*-amyl isomer formed a solid white precipitate immediately on mixing, melting point 91° C.

In experiments 10 and 22-24, the reaction product formed was analyzed. The irradiated liquid was distilled in a 25 ml. Claisen flask with a Vigreux column, and the fraction boiling over 100° C. was collected. This fraction was shaken with 20% AgNO₃ solution to precipitate any residual butyl mercaptan. The top layer was washed several times with distilled water, then shaken with 30% NaCl solution to remove excess Ag⁺ ions, and then washed again several times with distilled water. A 1.0 molar solution of HgCl₂ in 95% ethanol was added in a 2.5:1 ratio for the theoretical amount of amyl butyl sulphide formed. Immediately upon mixing, a white precipitate formed. The mixture was chilled in a refrigerator overnight. The white precipitate was filtered off and was dried over CaCl₂. Melting point: 89° C. After recrystallization from benzene and drying over P₂O₅, the melting point was 91° C. No evidence was obtained for the 2-amyl, *n*-butyl isomer.

In order to get a quantitative estimation of the amount of the *n*-butyl *n*-amyl sulphide formed it was necessary to determine the composition of the mercuric chloride addition product. Faragher, Morrell, and Comay (6) report the formation of three types of addition product: (R₂S)₂.HgCl₂, R₂S.HgCl₂, and R₂S.2HgCl₂, depending upon R and the medium from which the product was precipitated. They did not however report the formation of the addition product of *n*-butyl *n*-amyl sulphide.

Samples of the mercuric chloride addition product obtained from experiments 10 and 22-24 were analyzed, both before and after recrystallization, following a standard procedure (19):

10, before recrystallization:	56.3; 57.2% Hg
22-24, before recrystallization:	58.3; 58.7% Hg
10, after recrystallization:	60.5; 61.3% Hg
22-24, after recrystallization:	62.4; 62.4; 60.3% Hg

The calculated amounts of mercury in the 2:1, 1:1, and 1:2 mercuric chloride addition products are 33.8, 46.4, and 57.4%, respectively. From this it is concluded that the product obtained is C₉H₂₀S.2HgCl₂.

The amounts of the precipitate obtained, before recrystallization, in experiments 10 and 22-24 were 75 and 95%, respectively, of the theoretical amount. Thus the main reaction product is *n*-butyl *n*-amyl sulphide.

C. Yields

1. Energy Absorbed

The amount of energy absorbed in the various irradiation positions was measured using the Fricke dosimeter (21). 0.8 N H₂SO₄ solutions of 8.0×10⁻⁴ M./l. ferrous

ammonium sulphate were irradiated and the concentration of Fe^{3+} formed was determined using a Beckman DU spectrophotometer. Using a G -value of 15.5 (8, 21), 1 $\mu\text{M./l.}$ converted is equivalent to 6060 ergs/g. absorbed. The results are recorded in column 4 of Table I.

Owing to the difference in effective atomic number, the non-aqueous reaction mixture will not absorb the same amount of energy as the ferrous ammonium sulphate solution from 140 kvp. X-rays. The spectrum of the 140 kvp. source covers a region where absorption occurs through both the Compton effect and the photoelectric effect (11). The energy absorbed from an X or γ ray beam may be written as:

$$E_{ab} = F(\epsilon\mu_a)n,$$

in which E_{ab} is energy absorbed in ergs/g., F is incident energy flux in ergs/cm.², $\epsilon\mu_a$ is the real electronic absorption coefficient in cm.²/electron, and n is the number of electrons per gram. $\epsilon\mu_a$ may be split into a term for photoelectric absorption ($\epsilon\tau$), a term for Compton absorption ($\epsilon\sigma_a$), and a term for pair production absorption ($\epsilon\pi_a$).

$\epsilon\tau$ changes rapidly with the atomic number, depending approximately on Z^3 . $\epsilon\sigma_a$ is independent of the atomic number, Z , of the absorbing material. $\epsilon\pi_a$ is zero for the absorption from a 140 kvp. X-ray beam. Hence in the photoelectric effect region, the amounts of radiation absorbed by water and by the non-aqueous reaction mixture will be different. The behavior of different materials with respect to X-rays depends only on the atomic number of the constituents and is nearly independent of their state of chemical combination (11).

The effective atomic number \bar{Z}_L of the atoms in a compound for the photoelectric effect is defined (11) as

$$\bar{Z}_L = (a_1Z_1^3 + a_2Z_2^3 + a_3Z_3^3)^{\frac{1}{3}}$$

in which Z_1 = the atomic number of element 1,

$$\begin{aligned} a_1 &= \text{the fractional content of the electrons belonging to element 1,} \\ &= n_1/(n_1 + n_2 + n_3) \end{aligned}$$

where n_1 = number of electrons belonging to element 1.

Using this formula, we find for our reagents:

$$\bar{Z}_L(\text{C}_6\text{H}_{12}) = \left(\frac{36}{48}(6)^3 + \frac{12}{48}(1)^3 \right)^{\frac{1}{3}} = 5.45,$$

$$\bar{Z}_L(\text{C}_5\text{H}_{10}) = 5.45, \quad Z_L(\text{C}_4\text{H}_9\text{SH}) = 11.23, \quad \bar{Z}_L(\text{C}_6\text{H}_6) = 5.70, \quad \bar{Z}_L(\text{H}_2\text{O}) = 7.43, \\ \bar{Z}_L(0.8 \text{ N H}_2\text{SO}_4) = 7.68.$$

The \bar{Z}_L of the Fricke dosimeter solution may be considered to be equal to the \bar{Z}_L of 0.8 N H_2SO_4 , since the absorption by ferrous ammonium sulphate is negligible owing to its low concentration.

The reaction mixture in experiments 2-7 was 0.96 M./l. $\text{C}_4\text{H}_9\text{SH}$, 0.95 M./l. C_5H_{10} , and 7.36 M./l. C_6H_{12} . The number of electrons per molecule of these compounds is 50, 40, and 48 respectively. Hence the effective atomic number of the mixture $\bar{Z}_L(2-7)$ will be

$$\left(\frac{0.96 \times 50 \times 11.23^3 + 0.95 \times 40 \times 5.45^3 + 7.36 \times 48 \times 5.45^3}{0.96 \times 50 + 0.95 \times 40 + 7.36 \times 48} \right)^{\frac{1}{3}} = 6.69.$$

$$\text{Hence } \epsilon\tau(2-7) = (6.64/7.68)^3 \epsilon\tau(0.8 \text{ N H}_2\text{SO}_4) = 0.66 \epsilon\tau(0.8 \text{ N H}_2\text{SO}_4).$$

Relatively little work has been done with low energy X-ray machines on non-aqueous systems. To calculate the exact contribution of the photoelectric effect, the spectral distribution of the filtered radiation of the machine has to be known and calculations of this kind are not usually made in radiation chemistry. Forsyth, Weber, and Schuler (8) have made an approximate calculation similar to the one we are using. Chapiro, Boag, Ebert, and Gray (4) also show the importance of taking the photoelectric effect into account.

In order to get an approximate calculation for the radiation of the 140 kvp. source the radiation can be regarded as monochromatic radiation with the same half value layer (H.V.L.). The H.V.L. of the filtered radiation of the 140 kvp. source is 3.25 mm. Al. This corresponds to an equivalent kilovoltage of 36.7 kev. The equivalent kilovoltage of the beam irradiating the reaction mixture will be slightly higher, however, as it will be filtered through 3 mm. of lucite, 5 mm. of water, and the pyrex glass walls of the dilatometer. A value of 41 kev. is assumed for purposes of calculation. For water, $\epsilon\sigma_a$ is 17% and $\epsilon\tau$ is 83% of $\epsilon\mu_a$ at this energy (8). From this it may be calculated that the corresponding figures for 0.8 N H₂SO₄ are 16 and 84% respectively.

Since $\epsilon\sigma_a$ is independent of the atomic number, Z , of the absorbing material, the $\epsilon\sigma_a$ of the reaction mixture is equal to that of 0.8 N H₂SO₄, and since $\epsilon\tau(2-7) = 0.66\epsilon\tau(0.8 \text{ N H}_2\text{SO}_4)$, we may now write

$$\epsilon\mu_a(2-7) = (0.16 + 0.84 \times 0.66) \epsilon\mu_a(0.8 \text{ N H}_2\text{SO}_4) = 0.71 \epsilon\mu_a(0.8 \text{ N H}_2\text{SO}_4).$$

The numbers of electrons per gram of the reaction mixture and of the 0.8 N H₂SO₄ solution are approximately equal (3.40×10^{23} and 3.33×10^{23} respectively). Hence the values for the energy absorption by the Fricke dosimeter as given in Table I, column 4, have to be multiplied by 0.71 in order to obtain the real values for experiments 2-7.

Table I, column 5, gives the amount of radiation actually absorbed by the reaction mixture, as calculated above. All the experiments done with 0.96 M./l. C₄H₉SH mixtures absorb about the same amount of energy from the 140 kvp. beam, nearly independent of the 1-pentene concentration (compare Table I). Those experiments done with an amount of *n*-butyl mercaptan different from 0.96 M./l. will need to be corrected by a factor other than 0.71. For example, in experiments 22-24, in which the reaction mixture is 4.5 M./l. C₄H₉SH, 4.7 M./l. C₅H₁₀,

$$\epsilon\mu_a(22-24) = 1.72 \epsilon\mu_a(0.8 \text{ N H}_2\text{SO}_4).$$

So for experiment 22, where the rate of energy absorption for the ferrous ammonium sulphate solution was 18000 ergs/g./min.,* the rate of energy absorption for the reaction mixture is $18000 \times 1.72 = 31000$ ergs/g./min.

The above means that in experiments 15-19 (Fig. 4), which were done to determine the dependence of the reaction rate on the mercaptan concentration, the rate of energy absorption for each concentration is different. If we take as a standard the rate of energy absorption for a 0.96 M./l. C₄H₉SH solution, namely 25000 ergs/g./min. (Table I), equivalent to 19000 ergs/cc./min., then we can correct the observed reaction rates for the other concentrations to this value (from Fig. 2, rate is proportional to intensity in the present experiments). In Fig. 4, both the observed and the corrected rates are given.

The calculation of the absorption of energy by a reaction mixture differing in Z from 0.8 N H₂SO₄ is based on the assumption that the ratio of the amounts of energy absorbed is directly proportional to the ratio of the absorption coefficients of the two liquids. This

*180 rads/min.

is, strictly speaking, only true if the energy flux at any given point is the same for the two liquids; in other words, only if the attenuation of the photon beam by passing through a distance x of the one liquid is the same as by passing through a distance x of the other liquid. The error introduced into the calculated values of the energy absorbed, by neglecting this factor, may be shown to be less than 5%.

2. *G-Values*

From Fig. 5, 11.9 cm. contraction is equivalent to 1.5 M./l. C_4H_9SH converted. From this it follows that 1 cm. drop is equivalent to $1.5/11.9 = 0.126$ M./l. converted. For the calculation of G -values, this must be expressed in M./g.

In experiments 1 to 7, the concentration of the reactants is 0.96 M./l. C_4H_9SH , 0.95 M./l. C_6H_{10} , and 7.4 M./l. C_6H_{12} . Taking the densities of C_4H_9SH , C_6H_{10} , and C_6H_{12} to be 0.83, 0.64, and 0.78 respectively, the calculated density of the reaction mixture before irradiation is 0.77. The calculated increase in density after 4 cm. drop is only 1.3%. Thus, in the following calculation, the density is considered to be constant and equal to 0.775.

1 cm. drop is equivalent to 0.126 M./l. $= 0.126 \times 10^{-3}$ M./ml. $= 0.126 \times 10^{-3}/0.775 = 1.63 \times 10^{-4}$ M./g. converted. Fig. 2 shows that for experiments 2-7 an energy absorption rate of 300×10^3 ergs/g./min. results in a reaction rate of 0.092 cm./min. $= 0.092 \times 1.63 \times 10^{-4} = 1.50 \times 10^{-5}$ M./g./min. From this it follows that $1.50 \times 10^{-5}/300 \times 10^3$ moles are converted per erg absorbed, and as Avogadro's number $N = 6.02 \times 10^{23}$ and 1 erg $= 6.25 \times 10^9 \times 100$ ev., we find

$$\begin{aligned} G_{2-7} &= 1.50 \times 10^{-5} \times 6.02 \times 10^{23} / 300 \times 10^3 \times 6.25 \times 10^9 \\ &= 4.8 \times 10^4 \text{ molecules converted/100 ev. absorbed.} \end{aligned}$$

In experiments 21 to 24, in which only *n*-butyl mercaptan and 1-pentene were present, $G_{21-24} = 1.9 \times 10^5$. In experiments 25 and 26, which were carried out in benzene solution, $G_{25-26} = 1.5 \times 10^4$.

DISCUSSION

This study has shown that the addition reaction of *n*-butyl mercaptan to 1-pentene can be initiated by ionizing radiations. The reaction is similar in a number of respects to the reactions between mercaptan and olefin, initiated by oxidants or ultraviolet radiation. As in the photoinitiated reaction the main reaction product is the anti-Markownikow product, *n*-butyl *n*-amyl sulphide. The reaction is also a chain reaction, as evidenced by the high value for G ($> 10^4$). The radiation reaction also resembles the photoreaction in that it is inhibited by oxygen and that the inhibition time is markedly decreased by degassing the system.

Figs. 3 and 4 show the change in rate brought about by varying the pentene concentration at a constant butyl mercaptan concentration and vice versa. In both cases the curves level off at high concentrations, the curve for variable pentene levelling off at a higher rate than the one for variable mercaptan. The photochemical reaction shows a similar behavior (Fig. 6, Ref. 20) except that now the curve for variable butyl mercaptan levels off at a higher rate than the one for variable pentene.

In the radiation chemical reaction the chain initiating $C_4H_9S\cdot$ radical can be formed either by direct bond breakage of the SH bond in C_4H_9SH :



or in a number of different ways which may be represented symbolically as

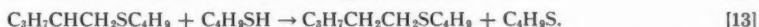


$R\cdot$ can be an H atom or any suitable radical formed by bond rupture by radiation. This may be represented symbolically as



In a further experiment a 0.96 M./l. *n*-butyl mercaptan, 0.95 M./l. 1-pentene solution in cyclohexane, which had not been deaerated, was irradiated during 115 minutes in a sealed dilatometer. No contraction of the reaction mixture could be observed during this period, agreeing with experiment 1, in which the inhibition period was about 120 minutes. During this period most of the oxygen present will have been used up by reactions such as [7]. After the irradiation, the amount of *n*-butyl mercaptan in the reaction mixture was determined with an amperometric titration. No mercaptan disappearance could be observed. It may therefore be concluded that most of the oxygen reacted with radicals other than $C_4H_9S\cdot$ radicals. From this it follows that the amount of initiation by direct bond breakage of the SH bond as given by equation [8] is negligible compared to the amount of initiation by equation [9].

The role of oxygen in a radiation chemical experiment in which the reaction mixture has not been deaerated is thus quite different from the role of oxygen in the corresponding photochemical experiment. In the radiation chemical reaction, reactions with oxygen supersede the initiation step (9). In the directly initiated photochemical reaction, reactions between oxygen and the free radical chain carriers must be thought to be responsible for the inhibitory action of oxygen (2). The reaction chain will be given by reactions paralleling reactions [1-3].



Thus, the marked similarity between photo- and radiation-initiated reactions is quite reasonable.

Fig. 2 (experiments 2-7 and 21-24) indicates that in these experiments the reaction rate is directly proportional to the rate of absorption of energy. This is in direct contrast to the behavior reported for the photochemical reaction by Back, Trick, McDonald, and Sivertz (2). Using solutions of approximately the same concentrations (0.975 M./l. C_4H_9SH , 0.975 M./l. C_5H_{10} , benzene as solvent) as in our experiments, they found the reaction rate to be proportional to the square root of the intensity.

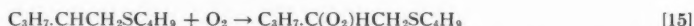
In looking for a possible explanation for this difference, it was pointed out that inhibitors were present, as evidenced by the inhibition period, and that inhibitors might be producing a different effect than in the photochemical reaction. The suggestion was then made that somewhat different results might be obtained in the radiation experiments if the reagents were given a more rigorous purification by thorough drying and degassing by distillation under vacuum. This, indeed, turned out to be the case. In fact, a careful removal of traces of oxygen gave a square root dependence on intensity as in the photochemical reaction (see following paper). This suggests that oxygen is relatively of more importance in the radiation reaction than in the photoreaction and is, in fact, playing a somewhat different role. This could well be the case, since the radicals present in the photo- and radiation-reactions differ. In the photoreaction the SH bond can be selectively split to give $RS\cdot$ radicals, whereas in the radiation reaction the radiation is not selectively absorbed but produces numerous different radicals, including radicals from the solvent and the pentene. The radiation also gives rise to electrons. Oxygen

might well react very differently with $RS\cdot$ than with the other radicals produced by ionizing radiations. (See above for the preferential reaction of oxygen with radicals other than $RS\cdot$.) It might also act as a scavenger for some of the electrons, producing O_2^- and leading to the production of peroxide radicals and HO_2 instead of $R\cdot$ and H .

Thus the observed linear dependence on dose rate could be explained by termination reactions such as [7] above, or



and



rather than [4], [5], and [6]. (For a further discussion, see Paper II in this series.)

Experiments 25 and 26, which were carried out under the same conditions as experiments 2 and 4 but with benzene instead of cyclohexane as solvent, show a lower reaction rate and G -value. This difference is probably due to the known protective effect of aromatic compounds against ionizing radiations (17).

ACKNOWLEDGMENTS

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ADDITION OF *n*-BUTYL MERCAPTAN TO 1-PENTENE ON IRRADIATION WITH X-RAYS OR GAMMA RAYS

II. EFFECT OF RIGOROUS DRYING AND DEGASSING¹

A. FONTIJN² AND J. W. T. SPINKS

ABSTRACT

Butyl mercaptan reacts with 1-pentene when irradiated with X and gamma rays. Experiments on mixtures which had been rigorously degassed and dried suggest that the reaction kinetics are strongly dependent on traces of oxygen in the system. A possible mechanism for the reaction is given.

INTRODUCTION

In the previous paper (4) the reaction of *n*-butyl mercaptan with 1-pentene on irradiation with X-rays has been described. A comparison with the corresponding photoinitiated reaction showed that while the reactions were in general rather similar they did differ in some respects, such as dependence on radiation intensity. Since the latter is commonly related to the mechanism of chain breaking, the possible effect of traces of impurities was investigated. This in turn led to an examination of the effect of rigorous degassing and drying of the reaction mixture.

EXPERIMENTAL METHODS

A. Chemicals

The chemicals used were the same and had the same degree of purity as for the earlier experiments reported in (4).

B. Radiation Source

The radiation source used was a 140 kvp. X-ray tube.

C. Dilatometers

The dilatometers used were the same as for the earlier experiments (4), and were cleaned in the same way as in the earlier experiments, except that after rinsing out with distilled water no acetone was used. Instead, the dilatometers were rinsed three more times with specially redistilled water, prepared in the same way as for ferrous sulphate dosimetry. The dilatometer was then attached to the vacuum line.

D. The Filling of the Dilatometers

Fig. 1 gives a picture of the vacuum line used. The dilatometer is shown attached to the vacuum line by a 10/30 ground glass joint. To the left of it are a measuring pipette, one 100-ml. and two 50-ml. round bottomed flasks, and an air inlet. To the right are a trap, a McLeod gauge, a manometer, an air inlet, a mercury diffusion pump, another trap, and a Cenco Hyvac pump, the latter not shown on the picture.

The 100-ml. round bottomed flask was filled with either cyclohexane or benzene. One 50-ml. flask was filled with *n*-butyl mercaptan, the other with 1-pentene. All flasks contained anhydron. The reagents were dried in this way for at least 24 hours and the line was then evacuated. While under vacuum the bulb of the dilatometer was heated with a

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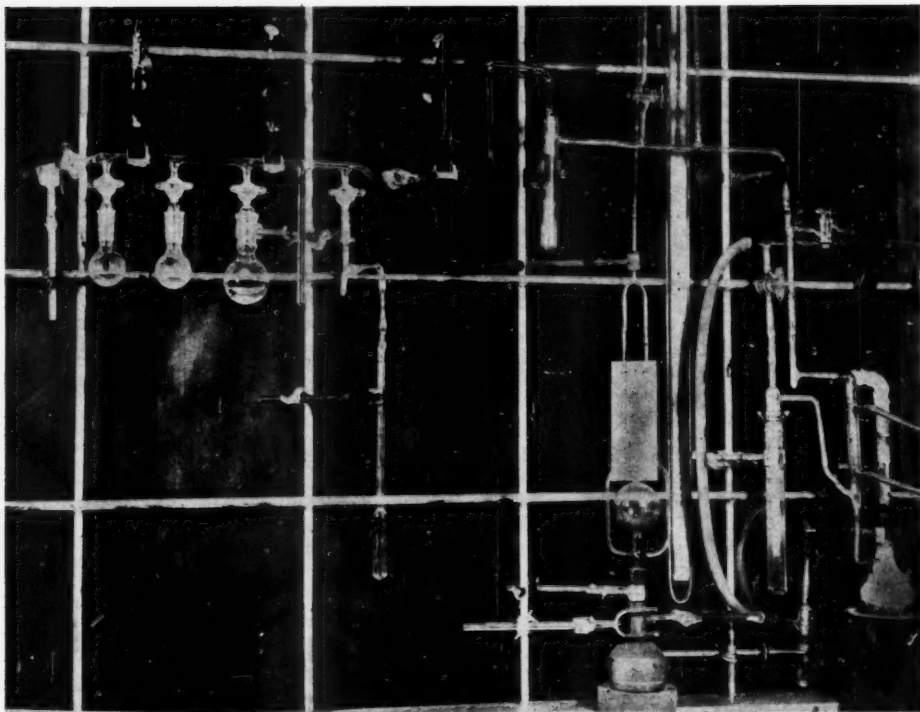


FIG. 1. Vacuum line used to degas reagents and fill dilatometer.

small flame and the capillary tube was treated by passing the high voltage, high frequency discharge of a Tesla coil through it (8).

The reagents were degassed one at a time by an alternate freezing and melting technique using liquid nitrogen. The stopcock between the right and left section of the vacuum line was then closed. The measuring pipette was immersed in a Dewar flask containing liquid nitrogen and the stopcock at the flask containing the mercaptan was opened. When the required amount of butyl mercaptan had distilled over, the container was closed off. The contents of the pipette then were distilled by this "cold finger" technique into the dilatometer. In the same way a measured amount of 1-pentene was brought into the dilatometer. The solvent was distilled directly from its container into the dilatometer. The mixture was degassed two or three more times and the dilatometer sealed off under vacuum. In this way a thoroughly dried and thoroughly degassed reaction mixture was obtained.

For experiments 18-21, a 10/30 ground glass joint was sealed onto the air inlet on the left side of the vacuum line. From a test tube attached to the 10/30 joint, water could be distilled into the reaction mixture.

All glassware used was cleaned with chromic acid cleaning solution.

E. The Irradiations

The dilatometers were irradiated in the same way as in the earlier experiments (4). The movement of the liquid meniscus was again followed using a cathetometer and the rate of energy absorption determined with ferrous sulphate dosimetry.

EXPERIMENTAL RESULTS

A. Observations

1. Reaction Rates

The reaction rate has again been taken as the slope of the linear part of the graph of centimeters' contraction versus minutes' irradiation. The results obtained are summarized in Table I. Two typical contraction-versus-time curves are given in Fig. 2.

In experiments 1-4, the reaction rate was determined for 0.96 M./l. *n*-butyl mercaptan, 0.95 M./l. 1-pentene solutions in cyclohexane at different rates of energy absorption using 140 kvp. X-rays. The observed rates are plotted in Fig. 3 against the square root of the rate of energy absorption. These results and those obtained for the same con-

TABLE I

SUMMARY OF REACTION RATES FOR IRRADIATION OF *n*-BUTYL MERCAPTAN AND 1-PENTENE IN CYCLOHEXANE SOLUTION AT 30° C., REAGENTS RIGOROUSLY DEGASSED AND DRIED, 140 KVP. X-RAYS

Experiment No.	Concentration		Rate of energy absorption, ergs/g./min. $\times 10^{-3}$		Reaction rate, cm./min.
	M./l. C_4H_9SH	M./l. C_5H_{10}	Measured ^a	Corrected ^b	
1	0.96	0.95	35	25	0.37
2	0.96	0.95	35	25	0.40
3	0.96	0.95	18	13	0.27
4	0.96	0.95	6	4	0.13
5 ^c	0.97	0.95	35	26	0.17
6	0.96	3.57	35	26	0.33
7	0.96	2.74	35	25	0.43
8	0.96	1.90	35	25	0.36
9	0.96	0.48	35	25	0.30
10	0.96	—	35	25	—
11	3.84	0.95	35	51	1.16
12	2.88	0.95	35	43	0.90
13	1.90	0.95	35	34	0.85
14	0.48	0.95	35	21	0.13
15	—	0.95	35	17	—

^aAbsorption as measured with the Fricke dosimeter.

^bThese doses corrected for the difference in effective atomic number between the reaction mixture and 0.8 N H_2SO_4 .

^cBenzene as solvent instead of cyclohexane.

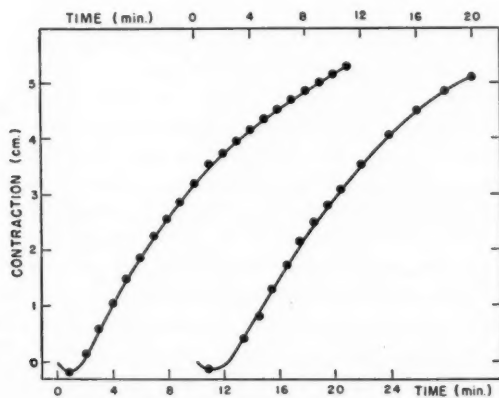


FIG. 2. Typical contraction-versus-time curve.

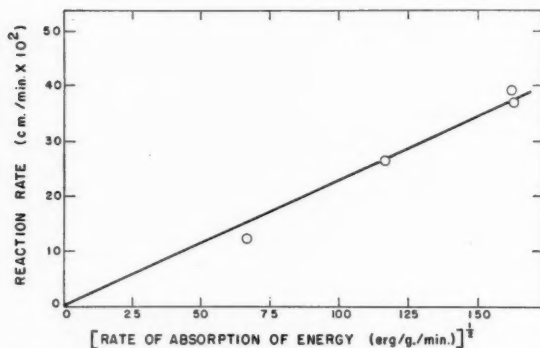


FIG. 3. Plot of reaction rate versus square root of rate of absorption of energy, 0.96 M./l. *n*-butyl mercaptan, 0.95 M./l. 1-pentene in cyclohexane.

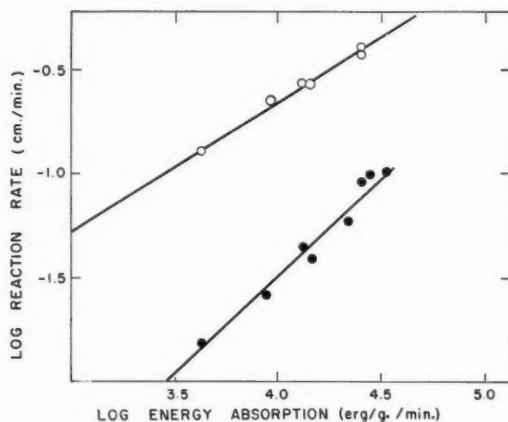


FIG. 4. Plot of logarithm of the reaction rate versus the logarithm of the rate of absorption of energy; data from earlier experiments (Ref. 4) are included for comparison purposes. \circ , present experiments; \bullet , earlier experiments.

centration with the earlier experiments 2-11 (4) are plotted in Fig. 4 as the logarithm of the reaction rate versus the logarithm of the dose rate.

In experiment 5 benzene was used as solvent instead of cyclohexane. The observed reaction rate is lower than the corresponding rate obtained with cyclohexane as solvent.

In experiments 6-10 the 1-pentene concentration was varied from the previous ones, the *n*-butyl mercaptan concentration being kept constant. In experiments 11-15, the *n*-butyl mercaptan concentration was varied. In this way, Figs. 5 and 6, giving the dependence of the reaction rate on the concentration, were obtained.

It may be noted that the contraction-versus-time curves (Fig. 2) differ from those obtained in the earlier experiments in that an appreciable decrease in rate starts after a smaller contraction has occurred, and in that the decrease in rate occurs more gradually.

2. "Draper" and Postirradiation Effects

In all experiments, except 4, it was noted that the liquid meniscus first rose before it

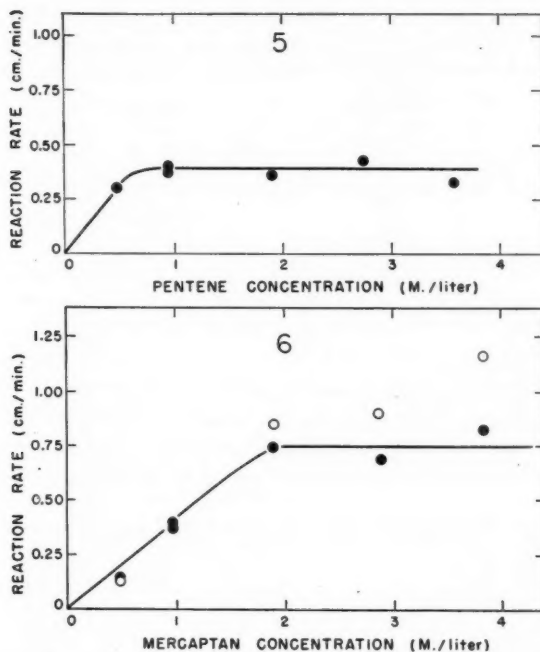


FIG. 5. Reaction rate as a function of the pentene concentration at constant butyl mercaptan concentration (0.96 M./l.) and a constant rate of energy absorption (19000 ergs/cc./min.).

FIG. 6. Reaction rate as a function of the butyl mercaptan concentration at constant pentene concentration (0.95 M./l.). O, observed values; ●, corrected to a constant rate of energy absorption (19000 ergs/cc./min.).

TABLE II
RELATION BETWEEN THE INITIAL RISE OF THE MENISCUS
AND THE REACTION RATE FOR A NUMBER
OF EXPERIMENTS

Experiment No.	Reaction rate, cm./min.	Maximum rise of the meniscus, cm.
11	1.16	0.375
7	0.43	0.230
1	0.37	0.170
3	0.27	0.065
4	0.13	—

dropped. This "Draper" type effect is in general the bigger the faster the reaction. This is illustrated by Table II. In all experiments the maximum rise was observed after about 1 minute irradiation.

No dark reaction previous to the irradiation could be observed. In all experiments a postirradiation effect could be noticed. The drop of the meniscus in the first minute after irradiation was always about as big as in the minute preceding it. After this first minute the drop rate rapidly decreased. As an example, the observations for experiment 11 are given in Table III. This postirradiation effect is likely an inverse Draper effect.

TABLE III
DATA FOR A TYPICAL IRRADIATION EXPERIMENT

Minutes irradiation	Drop, cm.
0	0
8	5.785
9	6.195*
10	6.450
12	6.575
20	6.575

*The irradiation was stopped after 9 minutes.

*B. Analysis**1. Mercaptan Disappearance*

The amount of butyl mercaptan present after irradiation, and thence, by difference, the butyl mercaptan disappearance, was again determined by an amperometric titration with silver nitrate. The results were in good agreement with the graph of centimeters' contraction versus mercaptan disappearance obtained for the earlier experiments (Fig. 5, (4)).

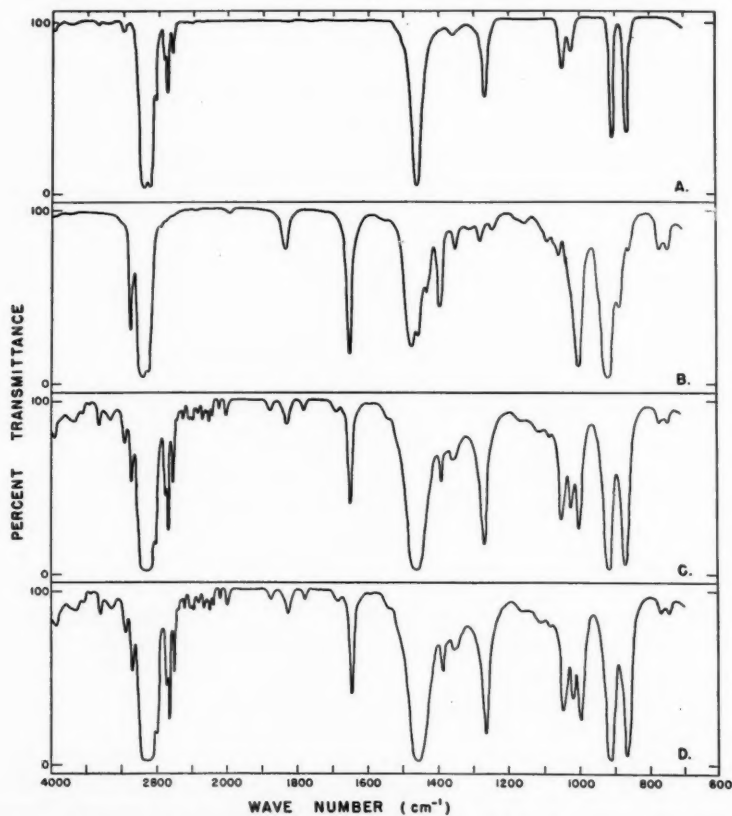


FIG. 7. Absorption spectra: A, cyclohexane; B, 1-pentene; C, 1.0 M./l. 1-pentene in cyclohexane; D, same as C, irradiated 40 minutes at 17000 ergs/g./min.

2. The Reaction Product

Analysis for the reaction product was carried out for experiment 1. The same procedure as for the earlier experiments was followed. It was shown again that the main product was *n*-butyl *n*-amyl sulphide and that the amount formed was at least 61% of the theoretical yield.

3. Infrared Spectra

The progress of the reaction between *n*-butyl mercaptan and 1-pentene was also followed by infrared spectrophotometry.

A small vessel made of 10 mm. pyrex glass tubing was used in place of the usual dilatometer. The procedure followed for cleaning and vacuum filling of these vessels was the same as for the dilatometers. About 3.5 ml. of liquid was used for each experiment. The vessels were placed in the same position in the water bath as the dilatometers. The energy absorbed during the irradiation will therefore be about the same. The vessels were cut open shortly before the infrared spectra were taken. A Perkin-Elmer, model 21, double beam, infrared spectrophotometer equipped with a rock salt prism was used with NaCl cells of 0.03 mm. and 0.11 mm. thickness, respectively.

The spectra obtained are given in Figs. 7-9. An index to the spectra is given in Table IV. The absorption bands were identified from (2).

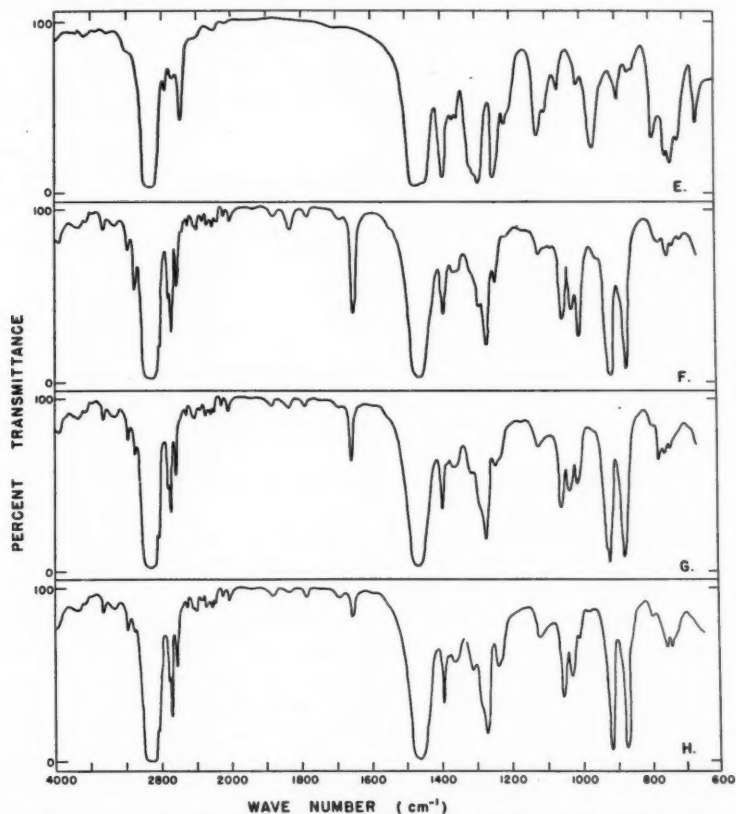


FIG. 8. Absorption in spectra: E, *n*-butyl mercaptan; F, 1.0 M./l. 1-pentene, 1.0 M./l. butyl mercaptan in cyclohexane; G, as in F, irradiated 13 minutes at 25000 ergs/g./min.; H, as in F, irradiated 60 minutes at 25000 ergs/g./min.

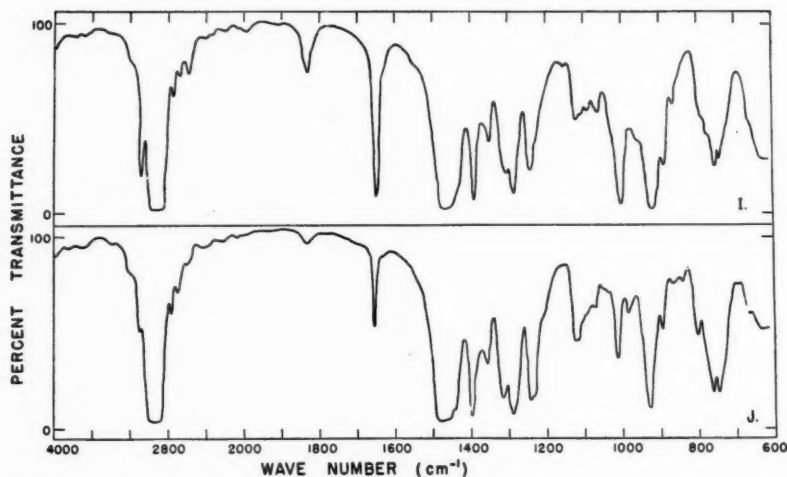


FIG. 9. Absorption spectra: I, 4.6 M./l. 1-pentene, 4.6 M./l. *n*-butyl mercaptan; J, same as I, irradiated 14 minutes at 60000 ergs/g./min.

TABLE IV
INDEX TO SPECTRA

Spectrum	Absorption cell thickness, mm.	Sample	Rate of energy absorption, ergs/g./min. $\times 10^{-3}$	Irradiation time, min.
A	0.03	Cyclohexane	—	—
B	0.03	1-Pentene	—	—
C	0.11	1.0 M./l. 1-pentene in cyclohexane	—	—
D	0.11	1.0 M./l. 1-pentene in cyclohexane	17	40
E	0.11	<i>n</i> -Butyl mercaptan	—	—
F	0.11	1.0 M./l. 1-pentene, 1.0 M./l. <i>n</i> -butyl mercaptan in cyclohexane	—	—
G	0.11	1.0 M./l. 1-pentene, 1.0 M./l. <i>n</i> -butyl mercaptan in cyclohexane	25	13
H	0.11	1.0 M./l. 1-pentene, 1.0 M./l. <i>n</i> -butyl mercaptan in cyclohexane	25	60
I	0.11	4.6 M./l. 1-pentene, 4.6 M./l. <i>n</i> -butyl mercaptan	—	—
J	0.11	4.6 M./l. 1-pentene, 4.6 M./l. <i>n</i> -butyl mercaptan	60	14

There are four absorption bands, due to the presence of the $-\text{CH}=\text{CH}_2$ group, which characterize the 1-pentene in these spectra. These are at:

3080 cm^{-1} : stretching vibration of ethylenic CH ,

1825 cm^{-1} : overtone of out-of-plane deformation vibration of ethylenic CH_2 ,

1640 cm^{-1} : stretching vibration of $\text{C}=\text{C}$,

990 cm^{-1} : out-of-plane deformation vibration of ethylenic CH .

Of these, the $\text{C}=\text{C}$ stretching vibration at 1640 cm^{-1} is the one most suitable for making a quantitative estimation of the amount of 1-pentene present, since it is a strong absorption band in a region in which there are no other absorption bands.

There is one relatively weak absorption band, due to the presence of the $-\text{S}-\text{H}$ group, through which the *n*-butyl mercaptan is characterized in these spectra. This is the SH stretching vibration at 2560 cm^{-1} .

Spectrum C was made from a 1.0 M./l. 1-pentene solution in cyclohexane, which

had not been irradiated. Spectrum D was obtained from a 1.0 M./l. 1-pentene solution in cyclohexane which had been irradiated. Since the two spectra are identical it may be concluded that the irradiation has caused no spectrophotometrically observable chemical change.

Assuming Beer's law to be valid, the optical density of an absorption band of a compound is proportional to its concentration. The optical density of an absorption band of a compound in a mixture can be determined by the "base line density method" in which the optical density at the base of an absorption peak is subtracted from the optical density at the peak.

Spectrum F was made from a 1.0 M./l. 1-pentene, 1.0 M./l. *n*-butyl mercaptan solution in cyclohexane. Spectrum G is of a solution of the same molarity, irradiated during 13 minutes at 25000 ergs/g./min. Spectrum H was obtained from a solution of the same molarity irradiated during 60 minutes at 25000 ergs/g./min. The optical density of the 1640 cm^{-1} peak of 1-pentene determined by the base line density method is for spectra F, G, and H: 0.41, 0.19, and 0.08, respectively. From this it follows that after 13 and 60 minutes irradiation 54 and 80%, respectively, of the 1-pentene has disappeared. The absorption peak of *n*-butyl mercaptan at 2560 cm^{-1} is too weak to be observable in these spectra. The amount of *n*-butyl mercaptan disappeared can however be evaluated by comparing with dilatometric experiment 1 which was carried out under similar conditions. After 13 minutes irradiation, in experiment 1, 3.52 cm. drop had occurred. According to Fig. 5, Ref. 4, this corresponds to a mercaptan disappearance of 46%. After 60 minutes irradiation 86% of the *n*-butyl mercaptan had disappeared. These figures are in good agreement with the supposed 1:1 reaction between 1-pentene and *n*-butyl mercaptan.

Spectrum I was made from an equimolar *n*-butyl mercaptan, 1-pentene mixture. Spectrum J was made from an equimolar mixture irradiated during 14 minutes at 60000 ergs/g./min. In this concentration the *n*-butyl mercaptan disappearance can be evaluated directly from the change in intensity of the *n*-butyl mercaptan peak at 2560 cm^{-1} . The base line density method gives, for Spectra I and J, respectively, an optical density of the 1640 cm^{-1} peak for 1-pentene of 1.25 and 0.27, and for the *n*-butyl mercaptan 2560 cm^{-1} peak of 0.070 and 0.020. From this it follows that 74% of the 1-pentene and 71% of the *n*-butyl mercaptan has disappeared after 14 minutes irradiation. These figures are again in good agreement with the supposed 1:1 reaction between 1-pentene and *n*-butyl mercaptan.

C. Yields

1. Energy Absorption

The energy absorbed by the reaction mixtures was calculated from the energy absorbed by the Fricke dosimeter in the same way as for the earlier experiments (4).

As was shown in (4) the rate of energy absorption of *n*-butyl mercaptan, 1-pentene solutions in cyclohexane, for a given position of the dilatometer relative to the radiation source, is dependent on the *n*-butyl mercaptan concentration but nearly independent of the 1-pentene concentration.

In experiments 11-15 (Fig. 6) the reaction rate is determined as a function of the *n*-butyl mercaptan concentration. Since the absorption of energy is different for each concentration a proper comparison between these experiments can only be obtained by correcting the observed reaction rates to those for a standard rate of energy absorption, bearing in mind that in the present series of experiments, the reaction rate is proportional

to the square root of the intensity. The rate of energy absorption of a 0.96 M./l. *n*-butyl mercaptan solution, 25000 ergs/g./min., has been taken as the standard rate. In Fig. 6 both the observed and the corrected reaction rates are given.

2. *G*-Values

The relation between the *n*-butyl mercaptan disappearance and the observed contraction in cm. is the same as for the earlier experiments (4). Therefore 1 cm. drop is again equivalent to 1.26×10^{-4} M./ml. converted.

The density of the reaction mixture in experiments 1-4 is 0.775. Thus, in these experiments, 1 cm. contraction is equivalent to $(1.26 \times 10^{-4})/0.775 = 1.63 \times 10^{-4}$ M./g. converted. For experiment 1, an energy absorption rate of 25000 ergs/g./min. results in a reaction rate of 0.365 cm./min. $\equiv 0.365 \times 1.63 \times 10^{-4} = 5.95 \times 10^{-5}$ M./g./min. From this it follows that $(5.95 \times 10^{-5})/25000$ moles are converted per erg absorbed, and since Avogadro's number $N = 6.02 \times 10^{23}$ and 1 erg = $6.25 \times 10^9 \times 100$ ev., we find $G_1 = (5.95 \times 10^{-5} \times 6.02 \times 10^{23})/(25000 \times 6.25 \times 10^9) = 2.3 \times 10^5$ molecules converted per 100 ev. absorbed.

In the present series of experiments the reaction rate is proportional to the square root of the rate of energy absorption. It follows therefore that *G* will differ for experiments which were carried out at the same concentration of the reactants but at a different dose rate, e.g. in experiment 4 a rate of absorption of energy of 4000 ergs/g./min. results in a *G*-value of 5.1×10^5 molecules converted per 100 ev. absorbed.

Experiment 5, in which benzene was used as solvent, gave a *G*-value of 9.1×10^4 molecules converted per 100 ev. absorbed.

3. Comparison with the Earlier Experiments

Although the reaction between *n*-butyl mercaptan and 1-pentene leads for both ways of filling the dilatometer to the same main reaction product *n*-butyl *n*-amyl sulphide, the kinetics of present experiments (in which the dilatometers were filled using a vacuum technique) differ from the earlier experiments (in which the dilatometers were filled using a funnel) in several aspects. In all experiments done in the present series the rate is higher than for the earlier experiments. The reaction rate is proportional to the square root of the intensity for the present experiments and directly proportional to the intensity for the earlier experiments. As before, the curves giving the reaction rate as a function of the concentration of one of the reactants, at a constant concentration of the other, level off at higher concentrations to a constant reaction rate independent of the concentration. In the present experiments, this constant reaction rate is about twice as big for high *n*-butyl mercaptan concentrations as for high 1-pentene concentrations, whereas for the earlier experiments the constant reaction rate for high 1-pentene concentrations was about twice as big as for high *n*-butyl mercaptan concentrations.

4. Effect of Added Impurities on the Reaction Rate

In the present experiments the reaction mixtures will presumably have a higher degree of purity than the reaction mixtures prepared by the simpler technique. In order to study the possible effect on the reaction rate of some of the impurities which may have been present in the earlier experiments, impurities were added to reaction mixtures prepared by the vacuum filling technique. In Table V the results obtained are summarized. The 140 kvp. source was used for all experiments.

The reagents in the earlier experiments had not been rigorously dried as compared to the reagents in the present experiments (in which the reagents had been dried over anhydron before they were distilled into the dilatometer). So, in experiments 16-19,

TABLE V
EFFECT OF IMPURITIES ON THE REACTION RATE FOR A NUMBER OF
EXPERIMENTS

Experiment No.	Concentration		Rate of energy absorption, ergs./g./min. $\times 10^{-3}$	Reaction rate, cm./min.
	M./l. C_4H_9SH	M./l. C_6H_{10}		
13 ^a	1.90	0.95	34	0.85
^b	1.91	0.95	34	0.080
16 ^c	1.90	0.95	34	0.86
1 ^a	0.96	0.95	25	0.37
2 ^a	0.96	0.95	25	0.40
^b	0.96	0.95	25	0.092
^b	0.96	0.95	25	0.088
17 ^c	0.96	0.95	25	0.32
18 ^d	0.96	0.95	25	0.30
19 ^a	0.96	0.95	25	0.28

^aNo impurities added.

^bEarlier experiments, as reported in Paper I (4).

^cWater saturated.

^dDilatometer not "degassed", further like ^c.

^eDilatometer treated with acetone and compressed air, further like ^d.

water, which had been previously redistilled once from alkaline permanganate and once from manganous hydroxide, was distilled into the dilatometer before the *n*-butyl mercaptan, 1-pentene, and cyclohexane were distilled in the usual way. The quantity of water added was 0.4 cc. in experiment 16 and 0.2 cc. in experiments 17-19. In this way a water-saturated reaction mixture was obtained, since a second liquid layer remained on the bottom of the dilatometer bulb even after it had been left at 30° C. and irradiated. Experiments 16 and 17 were otherwise filled with the usual vacuum technique. In experiment 18 the dilatometer was not "degassed" under vacuum by heating or by high voltage, high frequency discharge of a Tesla coil. In experiment 19 the dilatometer, after having been cleaned with chromic acid and rinsed with redistilled water, was washed with Merck reagent acetone following the procedure described in (4). Compressed air was then led through the dilatometer (compressed air had been used for drying the pipettes in the earlier experiments). The dilatometer was then attached to the vacuum line, evacuated, and filled.

It may be concluded from the reaction rates of experiments 16-19 that none of the impurities added are solely responsible for the difference between the present series of experiments and the earlier experiments. However, since the rate of reactions 17-19 is somewhat lower than for experiments 1 and 2 it is possible that some of these impurities were exerting some influence in the kinetics of the earlier experiments.

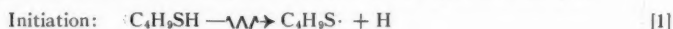
The method of filling in the present experiments would lead to a much more thorough degassing than in the earlier experiments and we are almost forced to conclude that a trace of oxygen is exerting an inhibiting effect in the earlier experiments. Oxygen has been reported as inhibiting the RSH-olefin reaction (3).

DISCUSSION

This study has shown that the kinetics for the reaction mixtures in the present series of experiments, in which the reaction mixtures were thoroughly degassed, differ in some respects from those for the previously reported reactions (4). In fact they show a greater similarity to the photoinitiated experiments.

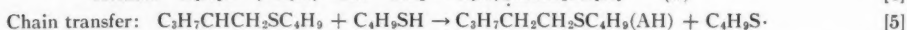
Fig. 3 indicates that in the present series of experiments the reaction rate is proportional to the square root of the rate of absorption of energy. The photoinitiated reaction also shows a square root dependence (1). The previously reported radiation-induced reaction, however, showed a direct proportionality (4). Figs. 5 and 6 show that the curves giving the dependence of the reaction rate on the concentration of one of the reactants, at a constant concentration of the other, level off at higher concentrations to a constant reaction rate independent of the concentration. In the present series of experiments this constant reaction rate is higher for high *n*-butyl mercaptan concentrations than for high 1-pentene concentrations, just as for the photoinitiated reactions (6). In the previously reported reactions the curve for high 1-pentene concentrations levelled off at a higher reaction rate than the curve for high *n*-butyl mercaptan concentrations (4).

The reaction scheme for the radiation-induced reaction can be given as in (4).



in which $R\cdot$ may be an H atom or a radical.

It was shown in (4) that where the reaction is carried out in cyclohexane solution, the amount of initiation through mechanism [1] is negligible compared to the amount of initiation through mechanisms [2] and [3].



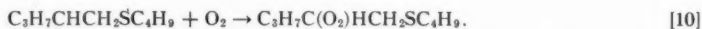
The square root dependence of the reaction rate on the rate of energy absorption observed in the present series of reactions is indicative of a mutual termination of the free radical chain carriers as the main termination step.



When the main termination step becomes a reaction between a free radical chain carrier and an entity other than a second free radical chain carrier, the reaction rate becomes proportional to the number of reaction chains and hence to the rate of initiation, which is itself proportional to the rate of absorption of energy. As stated before, the presence of traces of oxygen is thought to be the main cause for the difference between the present and the previous experiments. The main termination steps of the previously reported reactions may therefore be presumed to be:

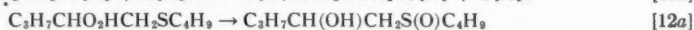


and

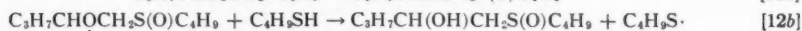


In this latter case, it has been suggested (5) that further reactions take place leading to the formation of hydroxylated sulphoxides.

Speculative mechanisms for these reactions are:



and/or



As the termination with oxygen supersedes the mutual termination of the free radical chain carriers it would be expected that the chain length in the previously reported experiments would be shorter than in the present series of experiments. Hence, the same initiation rate would result in a smaller reaction rate for the previously reported reactions than for the present series of experiments. This is in agreement with the observations.

In the photoinitiated experiments the reaction rate was found to be proportional to the square root of the rate of initiation for systems which had not been thoroughly degassed (1). It must therefore be presumed that the rate of initiation for the photochemical experiments was much higher than for the radiation chemical experiments; this would result in a higher concentration of free radical chain carriers which might then terminate mainly through mutual termination notwithstanding the presence of oxygen. Since the reaction rate of the present series of experiments is of the same order as in the photoinitiated experiments, and the rate of initiation in the present experiments is presumed to be lower than in the photoinitiated experiments, it follows that the kinetic chain length must be greater.

In the photoinitiated reaction, chain lengths of over 10^4 have been observed for low rates of initiation (1). There is no direct observation of the chain length in the radiation-induced reaction. However, it is possible to determine a minimum value from the observed G -values. In the present series of reactions it has been calculated that for experiment 1, for-example, G is 2.3×10^5 . In other words 2.3×10^5 molecules of C_4H_9SH have disappeared for every 100 ev. absorbed. For several organic liquids the number of primary free radicals formed per 100 ev. absorbed, $G(R)$, has been determined with DPPH and other methods (7). $G(R)$ values varying from 1 to 60 have been observed. The minimum possible value for the kinetic chain length in experiment 1 therefore is $(2.3 \times 10^5)/60 = 4 \times 10^3$. It is most likely that the $G(R)$ value of the reaction mixture will be lower than 60. Furthermore, only a small part of the free radicals formed in reaction [2] will react according to reaction [3] to form $C_4H_9S\cdot$ radicals and thus to initiate chains. The chain length of the radiation-induced reaction, therefore, will be of the same order or bigger than that of the photoinitiated reaction.

ACKNOWLEDGMENTS

Grateful acknowledgment is made to the National Research Council for continued financial support and for the award of a Postdoctoral Fellowship to one of us (A. F.). We are also grateful to Miss A. Epp for the determination of infrared spectra.

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ADDITION OF *n*-BUTYL MERCAPTAN TO 1-PENTENE ON IRRADIATION WITH X-RAYS OR GAMMA RAYS

III. ENERGY DEPENDENCE, 140 KVP. TO 24.5 MEVP.¹

A. FONTIJN² AND J. W. T. SPINKS

ABSTRACT

The effect of energy variation on the addition of *n*-butyl mercaptan to 1-pentene has been studied using radiations at 140 kvp., 1.25 Mev., and 24.5 Mevp. No appreciable energy dependence has been found over this range.

INTRODUCTION

Previous papers (2, 3) in this series have described the addition of *n*-butyl mercaptan to 1-pentene on irradiation with X-rays. This paper discusses the effect of energy variation from 140 kvp. to 24.5 Mevp.

EXPERIMENTAL METHODS

Use was made of a 140 kvp. X-ray machine, a telecurie Co⁶⁰ source (1.25 Mev.), and a betatron of 24.5 Mev. peak energy.

Irradiations of the butyl mercaptan - pentene mixture were carried out in a dilatometer, the dilatometer bulb being immersed in a thermostat fitted with a 1/16 inch lucite window through which the ionizing radiation entered (2). The outside of the dilatometer bulb was about 1/2 cm. behind the window. Thus, for 140 kvp. and Co⁶⁰ irradiations, the material surrounding the reaction mixture is thick enough to obtain electronic equilibrium. For the betatron irradiations a 4-cm. block of lucite was put in front of the lucite window.

The intensity of the radiation received by the reaction mixture could be changed by varying the distance between the radiation source and the water bath.

EXPERIMENTAL RESULTS

The effect of energy variation was investigated by irradiating mixtures of a given composition with radiations of two different energies chosen from 140 kvp., 1.25 Mev., and 24.5 Mevp. Mixtures which had been prepared according to the method described in Ref. 2 were used as well as those which had been more rigorously degassed and dried (3). Mixtures of the pure liquids were irradiated (4.5 M./l. butyl mercaptan, 4.7 M./l. pentene) as well as solutions in cyclohexane (0.96 M./l. butyl mercaptan, 0.95 M./l. pentene). The temperature was 30° C. The results obtained with the cobalt source and the betatron are summarized in Table I; those obtained with the 140 kvp. source are summarized by (2, 3). In Fig. 1 the reaction rate is plotted versus the rate of absorption of energy for mixtures prepared by the method of Ref. 2. Fig. 2 records the results, for rigorously degassed and dried mixtures, as rate of reaction versus the square root of the rate of energy absorption. The agreement between the results for the three radiation sources is within experimental error and indicates that there is no energy dependence over the range 140 kvp. to 24.5 Mev. peak for either system.

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TABLE I

SUMMARY OF REACTION RATES FOR IRRADIATION OF *n*-BUTYL MERCAPTAN AND 1-PENTENE IN CYCLOHEXANE SOLUTION AT 30° C.

Experiment No.	Concentration		Rate of energy absorption, ergs/g./min. $\times 10^{-3}$	Radiation source	Reaction rate, cm./min.
	M./l. C_4H_9SH	M./l. C_5H_{10}			
1 ^a	0.96	0.95	28	Co ⁶⁰	0.098
2 ^a	0.96	0.95	23	Co ⁶⁰	0.058
3 ^a	0.96	0.95	15	Co ⁶⁰	0.039
4 ^a	0.96	0.95	9	Co ⁶⁰	0.029
5 ^{a,b}	4.5	4.7	18	Betatron	0.19
6 ^{a,b}	4.5	4.7	18	Betatron	0.20
7 ^{a,b}	4.5	4.7	10	Betatron	0.12
8 ^c	0.96	0.95	14	Betatron	0.27
9 ^c	0.96	0.95	10	Betatron	0.23

^aDilatometers filled as described in Ref. 2.^bNo solvent.^cDilatometers filled as described in Ref. 3.

ENERGY ABSORPTION

The amount of energy absorbed in the various irradiation positions was measured using the Fricke dosimeter (2). For 140 kvp. radiation, absorption will be partly by photoelectric and partly by Compton processes. This means that the reaction mixture will absorb an amount of energy different from that absorbed by the dosimeter. The data given in Figs. 1 and 2 have been suitably corrected to allow for this difference. Details of the calculations are given in (2).

For Co⁶⁰ radiation at 1.25 Mev., absorption will be of the Compton type. It is independent of the atomic number, Z , of the absorbing material, and is proportional to the number of electrons per gram of the absorbing material. This number is practically independent of the materials used in these experiments (H_2O , 3.34×10^{23} ; C_4H_9SH , 3.30×10^{23} ; C_5H_{10} , 3.43×10^{23} ; C_6H_{12} , 3.43×10^{23} electrons per gram) and thus, for 1.25 Mev., the energy absorbed per gram of the solution of the Fricke dosimeter will be equal to the energy absorbed per gram of the reaction mixture.

For betatron X-rays, absorption is partly by Compton effect and partly by pair production. The amount of energy absorbed by the reaction mixture may be calculated from the amount of energy absorbed by the 0.8 *N* H_2SO_4 solution of the Fricke dosimeter by a method similar to the one used for 140 kvp. X-rays (2). The energy absorbed from the X-ray beam may again be written as

$$E_{ab} = F(\epsilon\mu_a)n$$

in which E_{ab} is energy absorbed in ergs./g., F is incident energy flux in ergs/cm.², $\epsilon\mu_a$ is the real electronic absorption coefficient in cm.²/electron, and n is the number of electrons per gram. $\epsilon\mu_a$ may be split up into three terms:

$$\epsilon\mu_a = \epsilon\tau + \epsilon\sigma_a + \epsilon\pi_a.$$

The contribution from the photoelectric term $\epsilon\tau$ can be neglected for betatron X-rays. The Compton term, $\epsilon\sigma_a$, is independent of the atomic number, Z , of the absorbing material. The pair production term $\epsilon\pi_a$ is proportional to the atomic number of the absorbing material. The effective atomic number for the pair production effect is given by

$$\bar{Z}_H = a_1Z_1 + a_2Z_2 + a_3Z_3,$$

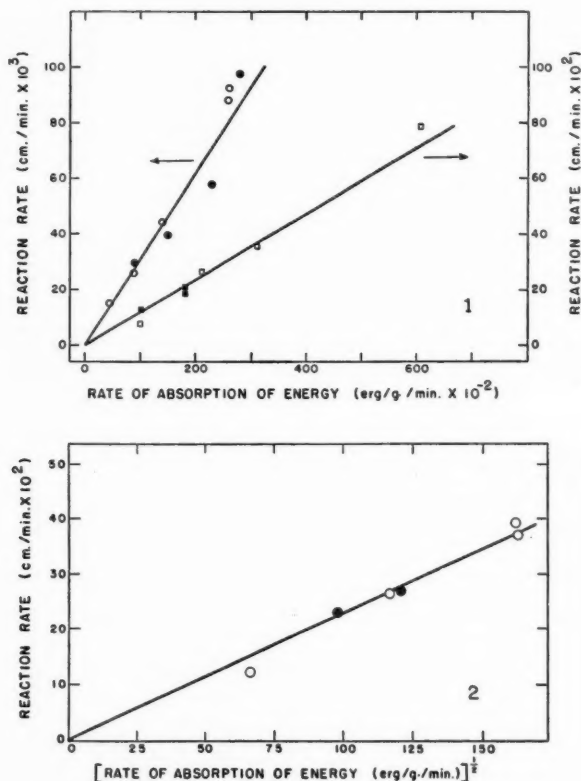


FIG. 1. Reaction rate versus rate of absorption of energy, earlier experiments, reaction mixtures not rigorously degassed (2): 4.5 M./l. butyl mercaptan, 4.7 M./l. 1-pentene; betatron ■; 140 kvp. X-rays, □; 0.96 M./l. butyl mercaptan, 0.95 M./l. 1-pentene; Co⁶⁰ gamma rays, ●; 140 kvp. X-rays, ○.

FIG. 2. Reaction rate versus square root of rate of absorption of energy, later experiments, reaction mixtures rigorously degassed (3): 4.5 M./l. butyl mercaptan, 4.7 M./l. 1-pentene; betatron, 24.5 Mev. peak, ●; 140 kvp. X-rays, ○.

in which a_1 is the fractional content of electrons belonging to element 1.

$$\bar{Z}_H(C_4H_9SH) = (24/50)6 + (10/50)1 + (16/50)16 = 8.20,$$

$$\bar{Z}_H(C_8H_{10}) = 4.75, \quad \bar{Z}_H(C_6H_{12}) = 4.75, \quad \bar{Z}_H(H_2O) = 6.60, \quad \bar{Z}_H(0.8 N H_2SO_4) = 6.73.$$

The reaction mixture in experiments 5-7 is 4.5 M./l. C_4H_9SH and 4.7 M./l. C_8H_{10} . The number of electrons per molecule of these compounds is 50 and 40 respectively. Hence

$$\bar{Z}_H(5-7) = (4.5 \times 50 \times 8.20 + 4.7 \times 40 \times 4.75) / (4.5 \times 50 + 4.7 \times 40) = 6.63,$$

$$\epsilon\pi_a(5-7) = (6.63/6.73)\epsilon\pi_a(0.8 N H_2SO_4) = 0.99\epsilon\pi_a(0.8 N H_2SO_4).$$

For a 0.8 N H_2SO_4 solution the percentage of energy absorbed as a result of the Compton effect and the percentage absorbed through pair production is 79 and 21%, respectively, as calculated using real electron absorption coefficients weighted according

to the modified Schiff photon distribution curve for 24.5 Mevp. X-rays. The curve had been modified from the theoretical Schiff curve for the absorption of the donut and monitor using total absorption coefficients and for the absorption by an 8-cm. lucite block surrounding the reaction mixture using real absorption coefficients. (For detail of calculation see (4).)

Since $\epsilon\mu_a$ is proportional to E_{ab} it follows that for a 0.8 N H_2SO_4 solution $\epsilon\sigma_a = 0.79\epsilon\mu_a$ and $\epsilon\pi_a = 0.21\epsilon\mu_a$, in which $\epsilon\mu_a$, $\epsilon\sigma_a$, and $\epsilon\pi_a$ are effective absorption coefficients for the betatron spectrum, and since $\epsilon\pi_a(5-7) = 0.99\epsilon\pi_a(0.8\text{ N } H_2SO_4)$, we may now write

$$\epsilon\mu_a(5-7) = (0.79 + 0.21 \times 0.99)\epsilon\mu_a(0.8\text{ N } H_2SO_4) = \epsilon\mu_a(0.8\text{ N } H_2SO_4).$$

This means that the reaction mixture of experiments 5-7 absorbs the same amount of energy from the betatron beam as the ferrous sulphate dosimeter placed in the same position.

For experiments 8 and 9, one finds in the same way $\epsilon\mu_a(8-9) = 0.95\epsilon\mu_a(0.8\text{ N } H_2SO_4)$.

DISCUSSION AND CONCLUSIONS

The foregoing has established that there is no appreciable energy dependence for the system from 140 kvp. to 24.5 Mevp. This is in agreement with the results for a number of other systems such as the oxidation of ferrous sulphate, reduction of ceric sulphate, and the radiolysis of chloroform and chloral hydrate (for a summary see (5)). The result is not unexpected since secondary electrons are produced in each case, with resulting electron and ion densities probably differing not too widely. Energy dependences which have been reported from time to time have usually been associated with widely differing ion densities (1, 5).

ACKNOWLEDGMENTS

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A RECORDING SPOON GAUGE¹

J. G. HOOLEY

ABSTRACT

The movement of the tip of a glass spoon gauge is followed by means of a linear variable differential transformer with a sensitivity of 2.2 mv. per micron. For a spoon that will stand a differential pressure of one atmosphere this amounts to 5 mv. per mm. of mercury. There is no hysteresis, the temperature coefficient is 0.1 mm. per °C., and there is a null point drift of about 0.05 mm. per hour. The over-all accuracy is 0.2 mm. in the range 0 to 760 mm.

INTRODUCTION

The pressure of a gas corrosive to mercury can be measured by observing the position of the tip of a spoon gauge with a travelling microscope. This article describes a more sensitive method of following and of recording the position of the tip. This is done by suspending the steel core B (Fig. 1) of a linear variable differential transformer C from

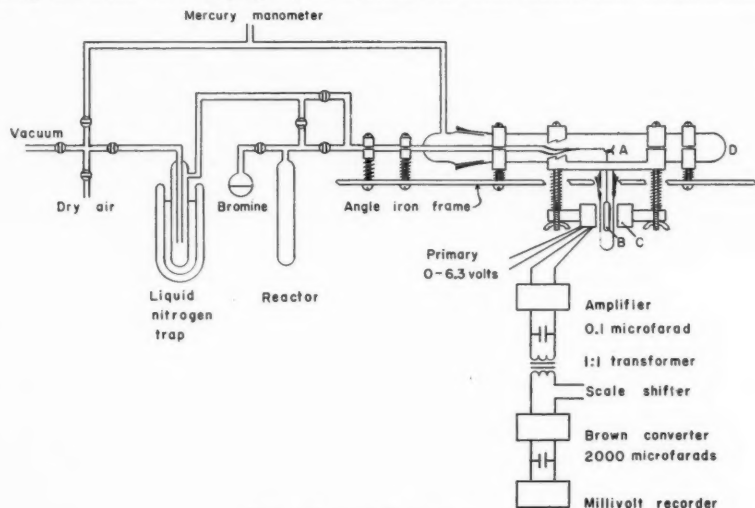


FIG. 1. Recording spoon gauge.

the tip A of the spoon. The transformer has one primary and two secondaries in opposition to one another. As the tip moves in response to a varying pressure difference between the envelope and the inside of the spoon, the steel core moves and the output of the transformer changes. This output is amplified, converted to d-c., and fed into a millivolt recorder. The circuit is the same as the one used for the recording vacuum thermobalance described previously (1). In fact, one can record pressure or weight on the same chart by using appropriate switches.

OPERATIONAL DETAILS

The envelope D is removed and a spoon is sealed to the inlet tube so that the tip A will be directly over the side arm. The envelope is replaced and the elevations of the

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Contribution from the Department of Chemistry, University of British Columbia, Vancouver, B.C., with financial assistance from the National Research Council.

four brass clamps holding it and the inlet tube are adjusted so that no strain results when the clamps are tightened. The adjustment is relative to a sturdy angle iron frame which holds the two adjusting screws and springs below each clamp. The transformer clamp is then attached to the envelope so that the transformer will be directly under the tip of the spoon. The core B is suspended with a soft glass rod and its envelope is placed in position. Both sides of the gauge are evacuated and the height of the transformer is adjusted with the two wing nuts so that the output voltage is about zero. The recorder controls are set so that this occurs with the pen near the center of the chart. This reading is the null point for zero pressure and is checked at regular intervals.

The spoon is then calibrated by measuring the output voltage as a function of pressure differential. With this sensitivity one can now calculate an unknown pressure in the spoon from the voltage reading that it produces and the pressure in the envelope as measured by a mercury manometer.

PERFORMANCE

Sensitivity

The data in this and in the following two sections are for a spoon that would stand a differential pressure of one atmosphere and which had a sensitivity of 5 mv. per mm. of mercury for an input voltage to the transformer of 1.6 v. and an amplifier setting of 40 db. This amounts to a sensitivity of 2.2 mv. per micron movement of the tip. Spoons of sensitivities up to 50 mv. per mm. of mercury for the same input voltage were made but they would not stand as high a pressure differential. The above sensitivities could theoretically be multiplied by four by raising the input voltage to its maximum of 6.3 v. It was found however that above 2 v. the magnetic field of the transformer prevented the centering of the core.

Fig. 2 shows that the output voltage is a linear function of the pressure differential from -10 to +65 cm. and that there is no hysteresis. These data are for the lower

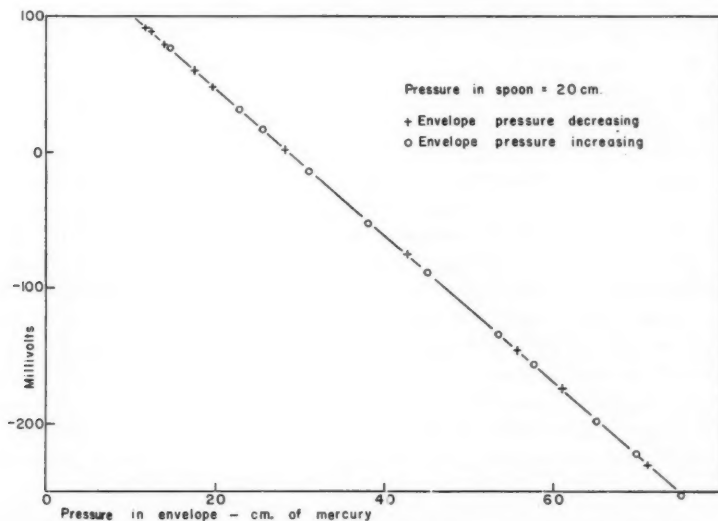


FIG. 2. Output voltage as a function of pressure differential.

input voltage of 0.18 v. so that the whole range of 75 cm. could be measured without changing the pressure in the envelope. Repeated determinations of sensitivity show a range of $\pm 5\%$.

Null Point

There is a gradual change of the output voltage for zero pressure differential amounting to about 0.05 mm. of mercury per hour. The direction of the change shows that the weight of the core is sagging the spoon. It is therefore necessary to redetermine the null point at regular intervals. This can be done during a run by turning the appropriate taps to seal off the reactor so that the spoon and its envelope can both be evacuated.

Temperature Coefficient

Theoretically the 11 cm. iron bolt in the transformer support and the 13 cm. soft glass rod holding the core will have a net coefficient of 0.4μ per $^{\circ}\text{C}$. This amounts to 0.8 mv. per $^{\circ}\text{C}$. and becomes noticeable when room temperature changes by more than a degree. It is automatically compensated for whenever the null point is redetermined.

DISCUSSION

The fact that the sensitivity is only reproducible to $\pm 5\%$ means that measurements should be made as close to the null point as possible. For instance, if one keeps within 10 mv. of this value the maximum error in pressure would be 0.1 mm. The other errors arise from glass flow under stress and from temperature effects. They are minimized by carefully following any changes in the null point. The over-all attainable accuracy in the range 0 to 760 mm. of mercury is about 0.2 mm.

The above gauge has been in use for 3 months recording bromine pressures up to 20 cm. The taps in the auxiliary system are greased with Kel-F and will still hold a vacuum of 0.001 cm.

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REARRANGEMENT STUDIES WITH C¹⁴

V. THE SOLVOLYSIS OF 2-PHENYLETHYL-1-C¹⁴ *p*-TOLUENESULPHONATE¹

C. C. LEE, G. P. SLATER, AND J. W. T. SPINKS

ABSTRACT

The solvolysis of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate in absolute ethanol, glacial acetic acid, 90% formic acid, and anhydrous formic acid gave rise to products which showed rearrangements of the C¹⁴-labeled atoms from the C-1 to the C-2 positions to the extent of 0.3%, 5.5%, 40%, and 45%, respectively. The results constitute an unequivocal proof that phenyl participation occurs in the reactions studied. The different degrees of rearrangement found for the different solvent systems are in agreement with the concept that the solvolysis process may have a range of mechanisms between the two extremes of the nucleophilic or S_N2 type and the limiting or S_N1 type. In the solvolysis in absolute ethanol, a small amount of "unreacted" 2-phenylethyl *p*-toluenesulphonate recovered from the reaction mixture was found to show isotope position rearrangement of almost the same degree as the ethanolysis product. This finding is tentatively attributed to the phenomenon of internal return involving an ethylphenonium *p*-toluenesulphonate ion-pair.

INTRODUCTION

The solvolyses of 2-phenylethyl, 2-*o*-anisylethyl, and 2-*p*-anisylethyl *p*-toluenesulphonates in ethanol, acetic acid, and formic acid have been investigated kinetically by Winstein and co-workers (18). From relative rate data, it was concluded that aryl participation in the rate-determining step of solvolysis is serious in the case of 2-*o*-anisylethyl and 2-*p*-anisylethyl *p*-toluenesulphonates in acetic and formic acid solvents. Unequivocal proof of neighboring aryl participation is obtainable with the use of the radioactive tracer technique. This paper reports observations on the solvolysis of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate. If neighboring phenyl participation were involved, the product of solvolysis should show a rearrangement of the C¹⁴-labeled atoms from the C-1 to the C-2 positions in the 2-phenylethyl system.

RESULTS AND DISCUSSIONS

2-Phenylethanol-1-C¹⁴ was obtained by the lithium aluminum hydride reduction of phenylacetic acid-1-C¹⁴ as previously reported (9). The *p*-toluenesulphonyl ester was prepared by treatment of the alcohol with *p*-toluenesulphonyl chloride in pyridine (14, 18). That all the C¹⁴-labeled atoms were located in carbon-1 of the 2-phenylethyl *p*-toluenesulphonate so prepared was shown by reaction of the ester with sodium iodide in acetone, yielding 2-phenylethyl iodide which, on oxidation with alkaline potassium permanganate, gave benzoic acid containing no radioactivity.

Solvolysis of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate was carried out in absolute ethanol, glacial acetic acid, commercially obtained 90% formic acid, and anhydrous formic acid, yielding, respectively, 2-phenylethyl ethyl ether, 2-phenylethyl acetate, and 2-phenylethyl formate for both formic acid solvents. The 2-phenylethyl ethyl ether was assayed for radioactivity and then oxidized to benzoic acid. Portions of the 2-phenylethyl acetate and formate were oxidized to benzoic acid and the remainder reduced with lithium aluminum hydride to give 2-phenylethanol which was converted to the *p*-nitrobenzoate derivative before being assayed for radioactivity. As phenyl participation during solvolysis would result in an isotope position rearrangement of the C¹⁴-labeled

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atoms from the C-1 to the C-2 positions in the 2-phenylethyl groups, the radioactivity in the benzoic acid samples derived from the various products of solvolyses is a measure of the degree of this rearrangement, the carboxyl carbon of the benzoic acid corresponding to C-2 of the original 2-phenylethyl radical. Results of radioactivity assays and degrees of rearrangement expressed as a percentage of the activity rearranging from C-1 to C-2 are tabulated in Table I.

TABLE I
RADIOACTIVITY DATA FOR SOLVOLYSIS OF 2-PHENYLETHYL-1-C¹⁴ *p*-TOLUENESULPHONATE

Reactant	Compound assayed	C.p.m. on a molar basis ^a		% Rearrangement	
		Run 1	Run 2	Run 1	Run 2
NaI in acetone	<i>p</i> -NO ₂ C ₆ H ₄ COOCH ₂ CH ₂ C ₆ H ₅ ^b	19650 ± 141			
	C ₆ H ₅ COOH	1 ± 7		0.0	
Absolute ethanol	CH ₃ CH ₂ OCH ₂ CH ₂ C ₆ H ₅	8687 ± 39	8653 ± 39		
	C ₆ H ₅ COOH	26 ± 7	16 ± 7	0.3	0.2
	C ₆ H ₅ COOH ^d	21 ± 7		0.2	
Glacial acetic acid	<i>p</i> -NO ₂ C ₆ H ₄ COOCH ₂ CH ₂ C ₆ H ₅ ^c	19747 ± 144	19841 ± 144		
	C ₆ H ₅ COOH	1089 ± 27	1076 ± 26	5.5	5.4
90% Formic acid	<i>p</i> -NO ₂ C ₆ H ₄ COOCH ₂ CH ₂ C ₆ H ₅ ^c	9285 ± 51	9294 ± 51		
	C ₆ H ₅ COOH	3783 ± 22	3743 ± 22	40.7	40.3
Anhydrous formic acid	<i>p</i> -NO ₂ C ₆ H ₄ COOCH ₂ CH ₂ C ₆ H ₅ ^c	9062 ± 51	9144 ± 51		
	C ₆ H ₅ COOH	4069 ± 23	4077 ± 23	44.9	44.7

^aAll compounds were converted to barium carbonate and counted as infinitely thick samples of constant geometry in a gas flow Geiger counter. Corrected for dilution by non-labeled carbon atoms by multiplying the observed activity with the number of carbon atoms per molecule in the compound assayed.

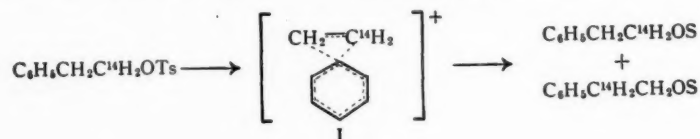
^bFrom the 2-phenylethanol used to prepare 2-phenylethyl-1-C¹⁴-*p*-toluenesulphonate.

^cFrom the 2-phenylethanol derived from solvolysis products.

^dDerived from the 2-phenylethyl *p*-toluenesulphonate recovered from the ethanolysis reaction mixture.

In the solvolysis of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate with absolute ethanol as solvent, about 12% of the sulphonate ester was recoverable from the reaction mixture after the reaction was allowed to proceed at reflux temperature for 2.5 days. The recovered ester was treated with sodium iodide in acetone and the resulting 2-phenylethyl iodide oxidized to benzoic acid. The radioactivity content of this sample of benzoic acid is also tabulated in Table I.

If phenyl participation in the solvolysis reactions studied were to involve an intermediate ethylphenonium ion (I), a 50% rearrangement of the C¹⁴-labeled atoms from positions C-1 to C-2 would be expected for the solvolysis product:



where OTs is an abbreviation for the *p*-toluenesulphonate (or tosylate) group and OS represents the conjugate base of the solvent.

From Table I, it can be seen that solvolyses in absolute ethanol, glacial acetic acid, 90% formic acid, and anhydrous formic acid gave, respectively, rearrangements of 0.3%, 5.5%, 40%, and 45%. These results indicate some phenyl participation in all the reactions studied; however, the results also show that the formation of I cannot be solely responsible for the entire course of the solvolysis reaction. The different amounts of rearrangements, or in other words, different degrees of phenyl participation, observed

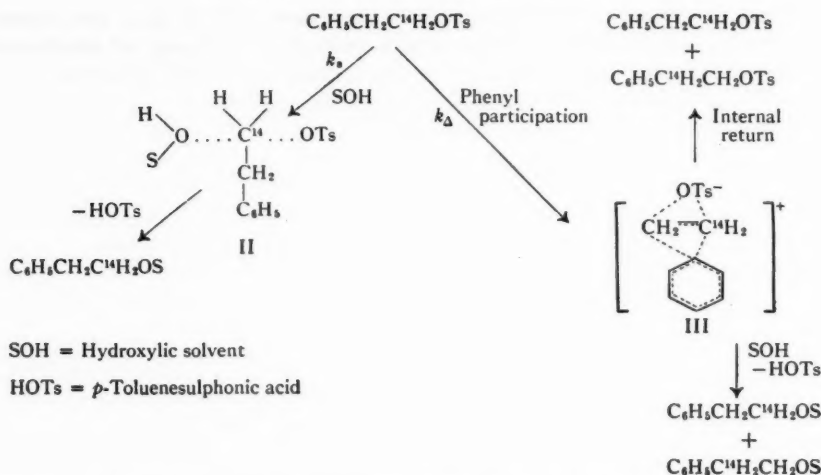
for the different solvents used are in agreement with the current view that the course of solvolytic reactions consists of a single process which may have a range of mechanisms between the two extremes of the nucleophilic or S_N2 type and the limiting or S_N1 type (12, 16). In the nucleophilic solvent ethanol the reaction proceeds predominantly by covalent attack by solvent or nucleophilic solvolysis. As a result, only a relatively small amount of rearrangement (0.2–0.3%) was found in the product of ethanolysis. In formic acid, a solvent of high ionizing power, the observed 45% rearrangement is the largest for the reactions investigated, indicating that formolysis proceeds to a great extent by anchimeric assistance from phenyl participation (18). In 90% formic acid, rearrangement somewhat lower than that for anhydrous formic acid was found. Apparently, the presence of some 10% water, a more basic solvent than formic acid, is sufficient to cause the change. With acetic acid, which is greatly inferior to formic acid in ionizing power (5) but less nucleophilic than ethanol (18), the 5.5% rearrangement observed implies that covalent attack by solvent is more important than phenyl participation for solvolysis in this solvent.

The "unreacted" 2-phenylethyl *p*-toluenesulphonate recovered from the ethanolysis mixture was also found to be rearranged by 0.2% (Table I). This small rearrangement, nearly the same as the degree of rearrangement in the ethanolysis product, likely arises from the process of internal return (2, 19). Phenyl participation in the solvolysis of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate may thus give rise to an ethylphenonium *p*-toluenesulphonate ion-pair which can "return" to yield 2-phenylethyl-1- C^{14} and 2-phenylethyl-2- C^{14} *p*-toluenesulphonates. Further experiments designed to show the possibility of ion-pair formation are underway. Preliminary tests indicated that when acetolysis is interrupted before completion, the recovered 2-phenylethyl *p*-toluenesulphonate also showed some isotope position rearrangement, substantiating the occurrence of internal return.

In accounting for the present experimental results, it is possible to devise a series of reactions involving structurally specific intermediates to show the course of the solvolysis of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate. In a manner somewhat analogous to the structural hypothesis of reaction intermediates advanced by Doering and Zeiss (3) and summarized by Streitwieser (12) for the interpretation of stereochemical behavior in solvolytic reactions, the following scheme is postulated for the solvolysis of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate.

More or less rearranged product of solvolysis may be formed depending on the relative amounts of phenyl participation or nucleophilic solvolysis, which would be governed by experimental conditions such as the ionizing power and nucleophilicity of the solvent. Nucleophilic solvolysis from covalent bonding between solvent and the sulphonate ester would result in a product without isotope position rearrangement. Phenyl participation is visualized as giving rise to an ethylphenonium *p*-toluenesulphonate ion-pair which can yield a product with the C^{14} -labeled atoms equally located in carbons 1 and 2. Internal return involving the ion-pair can also occur, resulting in the formation of 2-phenylethyl-1- C^{14} and 2-phenylethyl-2- C^{14} *p*-toluenesulphonates.

If we were to use the symbolism of Winstein and co-workers (17, 18), we can discuss the solvolysis of 2-phenylethyl *p*-toluenesulphonate in terms of two processes, one of them anchimerically assisted leading to III and the other anchimerically unassisted leading to II, with their respective rate constants designated k_A and k_s . The present data on isotope position rearrangements would lead to values for the ratio $k_A/(k_A + k_s)$ of 0.06, 0.11, 0.80, and 0.90 in absolute ethanol, acetic acid, moist formic acid, and dry



formic acid, respectively. These results are in excellent agreement with the conclusions of Winstein and Heck (17) that, in the solvolysis of 2-phenylethyl *p*-toluenesulphonate, relative rates and entropies of activation indicated that k was composed mainly of k_s in ethanol and acetic acid but consisted largely of k_Δ in formic acid.

EXPERIMENTAL

Reaction with Sodium Iodide in Acetone

A solution of 5 g. of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate and 3 g. of sodium iodide in 60 ml. of dry acetone was refluxed for 20 minutes and then allowed to stand at room temperature overnight. The resulting mixture was filtered and the precipitate washed with acetone. The combined filtrate and washings were poured into ice water, and a small amount of sodium bisulphite added to remove any coloration from free iodine. The aqueous mixture was extracted with ether and the extracts dried with anhydrous sodium sulphate. After removal of the ether from the dried extracts, 2-phenylethyl iodide, b.p. 112°C . at 12 mm. (lit. (9, 15) b.p. $115\text{--}118^\circ\text{C}$. at 14 mm., $114\text{--}116^\circ\text{C}$. at 12 mm.), was obtained by distillation under reduced pressure. The yield was 3.2 g. (76%).

Ethanolysis

The ethanol used was prepared from commercial absolute alcohol by refluxing with magnesium turnings to remove water and collecting the fraction boiling at 76°C . at atmospheric pressure (4).

Ten grams of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate and 100 ml. of dried ethanol were refluxed for 60 hours in a flask protected by a calcium chloride drying tube. Excess ethanol was distilled off and the residual liquid poured onto crushed ice. The aqueous mixture was made alkaline with potassium carbonate and extracted with ether. The ether extract was shaken twice with 20-ml. portions of saturated calcium chloride solution, washed with distilled water, and dried over anhydrous sodium sulphate and calcium chloride. The product, 2-phenylethyl ethyl ether, b.p. $77\text{--}78^\circ\text{C}$. at 10 mm. (lit. (13) b.p. $78\text{--}79^\circ\text{C}$. at 10 mm.), was recovered by distillation under reduced pressure. Anal. Calc. for $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5$: C, 79.9%; H, 9.38%. Found: C, 79.9%; H, 9.34%.

The residue in the distilling flask was dissolved in ether, treated with decolorizing

charcoal, and filtered through a Celite pad. The filtrate was evaporated to about 10 ml. and Skelly "C" was added dropwise until a faint cloudiness appeared in the solution. When the solution was cooled in ice, white crystals were deposited which were identified by mixed melting point (38°C.) as 2-phenylethyl *p*-toluenesulphonate. The weight of the recovered ester was 1.18 g. The yield of 2-phenylethyl ethyl ether (4.30 g.), based on the amount of sulphonate ester used, was 90%.

In a second run, 10 g. of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate gave 4.25 g. of 2-phenylethyl ethyl ether, 1.23 g. of the ester being recovered from the distillation residue.

The 2-phenylethyl *p*-toluenesulphonates recovered from both ethanolysis experiments were combined and treated with 1.3 g. of sodium iodide in 60 ml. of acetone. The yield of 2-phenylethyl iodide, b.p. 112°C. at 12 mm., was 1.7 g. or 83% of the theoretical.

Acetolysis

2-Phenylethyl-1- C^{14} *p*-toluenesulphonate (15.5 g.) was dissolved in 100 ml. of glacial acetic acid containing a sufficient amount of potassium acetate (6 g.) to neutralize the *p*-toluenesulphonic acid which might be produced. After the solution was refluxed for 20 hours, excess acetic acid was distilled off and the remaining liquid poured onto crushed ice. The aqueous mixture was made alkaline with potassium carbonate and extracted with ether. 2-Phenylethyl acetate was recovered from the dried ether extract by fractionation under reduced pressure. The fraction boiling at 109°C. at 18 mm. (lit. (7) b.p. $110\text{--}111^{\circ}\text{C.}$ at 18 mm.) was collected. The yield was 7.9 g. (86%).

A portion (2.1 g.) of the 2-phenylethyl acetate was reduced to 2-phenylethanol by lithium aluminum hydride. The yield was 1.3 g. (83%), b.p. 98°C. at 12 mm. (lit. (10) b.p. $98\text{--}100^{\circ}\text{C.}$ at 12 mm.). On treatment with *p*-nitrobenzoyl chloride (11), the 2-phenylethanol gave the corresponding *p*-nitrobenzoate, m.p. 62°C. (lit. (6) m.p. at $62\text{--}63^{\circ}\text{C.}$).

Formolysis

A mixture of 10.1 g. of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate, 4 g. of potassium formate, and 100 ml. of formic acid (90% or anhydrous) was refluxed for 20 hours. Excess formic acid was removed by distillation and the residue worked up as in the acetolysis. The yield of 2-phenylethyl formate, b.p. 73°C. at 3 mm. (lit. (1) b.p. $73\text{--}75^{\circ}\text{C.}$ at 3 mm.), ranged from 5.0 to 5.2 g. (90–93%). Portions of the 2-phenylethyl formate were also converted to 2-phenylethanol and then to the *p*-nitrobenzoate as described under acetolysis.

Oxidation Procedures

Samples of 2-phenylethanol, 2-phenylethyl acetate, and 2-phenylethyl formate were oxidized to benzoic acid using the method previously employed for the oxidation of 2-phenylethylamine (8). 2-Phenylethyl iodide and 2-phenylethyl ethyl ether were also oxidized to benzoic acid using the procedure previously described for the oxidation of 2-phenylethyl iodide (9).

ACKNOWLEDGMENT

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STUDY OF HALOGENATED HYDROXYPHENAZINES¹

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ABSTRACT

The properties of chlorotrihydroxydihydrophenazine were thoroughly investigated. Oxidations with sodium perborate or hydrogen peroxide in glacial acetic acid gave chlorotrihydroxyphenazine-5,10-dioxide. Methylation gave a monomethyl derivative and acetylation yielded mono-, di-, and tri-acetyl derivatives. Benzoylation gave a tetrabenzoyl compound. Bromination gave a monobromo derivative. Nitrosation produced a mononitroso and nitration a mononitro compound. Degradation by zinc dust distillation and thermal decomposition yielded phenazine. Molecular weight and absorption spectra determinations supported the chemical evidence that the compound was 1-chloro-2(or 3),6,8-trihydroxydihydrophenazine. 1,4,9-Trichloro-2(or 3),6,8-trihydroxydihydrophenazine, 1,4,9-trichloro-2(or 3, or 8),6-dihydroxydihydrophenazine, and 1-bromo-2(or 3),6,8-trihydroxydihydrophenazine were similarly identified.

INTRODUCTION

Chlorohydroxyphenazines have been prepared from the chloro derivatives by hydrolysis; for instance, 2,7-dichlorophenazine-5-oxide gave 2-hydroxy-7-chlorophenazine-5-oxide when refluxed with alcoholic potassium hydroxide (4). More recently, chlorotrihydroxydihydrophenazine, trichlorotrihydroxydihydrophenazine, trichlorodihydroxydihydrophenazine, and bromotrihydroxydihydrophenazine were prepared by reduction of halogenated nitrobenzenes (3).

In the present work, these halogenated hydroxyphenazines were further investigated and their structures elucidated. The study was considered to be of both theoretical and practical importance because the new compounds have possible uses as dyes, indicators, and antibiotics.

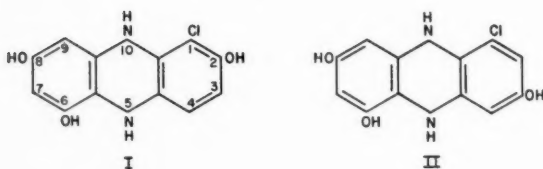
A detailed chemical study of chlorotrihydroxydihydrophenazine was made; it was reduced, oxidized, methylated, acetylated, benzoylated, brominated, nitrosated, nitrated, and finally degraded to phenazine. Also salts were prepared. Further study of the oxidation product, by decomposition, showed that the latter was a di-N-oxide. This evidence indicated that the parent compound was a dihydrophenazine. The only reactive group which could be detected in it was the phenolic hydroxyl group. Consequently, the three oxygen atoms were present in hydroxyl groups. There was no condensation with *o*-phenylenediamine; therefore there were no hydroxyl groups ortho to each other. Clemo and McIlwain (2) used this method to show that the two hydroxyl groups in iodinin were not in the 1 and 2 positions. Finally, the exact positions of the hydroxyl groups can be determined. Since 2,5-dichloronitrobenzene was reduced and gave analogues, trichlorohydroxydihydrophenazines, in which the 1, 4, and 9 positions were certainly occupied by chlorine atoms and the 6 position by a hydroxyl group, the 4 and 9 positions were thought to be free in the compound and the 1 position occupied by a chlorine atom and the 6 by a hydroxyl group. Two structures were possible, namely: 1-chloro-2,6,8-trihydroxydihydrophenazine (I) and 1-chloro-3,6,8-trihydroxydihydrophenazine (II):

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It was not possible to favor one structure over the other by chemical means because they are equivalent. Ultraviolet and infrared absorption spectral evidence supported the structures proposed. Therefore the compound was 1-chloro-(2 or 3),6,8-trihydroxydihydrophenazine.

Similar studies on the two trichloro analogues and the bromo analogue showed that the latter compounds were, respectively: 1,4,9-trichloro-2(or 3),6,8-trihydroxydihydrophenazine and 1,4,9-trichloro-2(or 3, or 8),6-dihydroxydihydrophenazine and 1-bromo-2(or 3),6,8-trihydroxydihydrophenazine.

ABSORPTION SPECTRA

The ultraviolet absorption spectra showed that the trichlorohydroxyphenazines studied were analogues of the chlorohydroxydihydrophenazine. A maximum absorption in the region of 270–285 $m\mu$ and a minimum at about 235–245 $m\mu$ were exhibited. The spectrum of the oxidation product of 1-chloro-2(or 3),6,8-trihydroxydihydrophenazine exhibited a maximum absorption at 304 $m\mu$; the introduction of the NO group caused a bathochromic shift. Ultraviolet absorption spectra are shown in Figs. 1 to 4.

Acetylation and formation of a sodium salt by the chlorotrihydroxydihydrophenazine indicated the presence of the OH group, and the formation of a hydrochloride and sulphate indicated the presence of the NH group. The infrared absorption spectrum shown in Fig. 5 confirmed these results; bands at 3430 cm^{-1} and 3370 cm^{-1} were assigned to these groups. The infrared absorption spectra of chlorotrihydroxydihydrophenazine and several of its derivatives were compared to the spectra of phenazine and phenazine-5,10-dioxide and to that of 1,6-dichlorophenazine, and similarities were noted as shown in Table II.

Chemical studies proved that the oxidation product of chlorotrihydroxydihydrophenazine was a di-N-oxide. The presence of strong bands at 812 cm^{-1} and 1098 cm^{-1} in the infrared spectrum given in Fig. 6 indicated the presence of the NO group. The spectrum of the oxidation product was found to be similar to that of 1-hydroxyphenazine-di-N-oxide, reported by Clemo and Daglish (1).

The bromotrihydroxydihydrophenazine was shown to be of analogous structure to the chlorotrihydroxydihydrophenazine by the fact that the infrared absorption spectra of these two compounds were almost identical, as illustrated in Fig. 7.

In the infrared spectrum of 1,6-dichlorophenazine shown in Fig. 8, a broad band at 686 cm^{-1} was assigned to the C—Cl bond which is present in the chlorophenazines studied in this work.

The infrared spectra of the triacetyl derivative of chlorotrihydroxydihydrophenazine and the monoacetyl derivative of trichlorodihydroxydihydrophenazine exhibited a strong band at 1790 cm^{-1} and this was attributed to the CO group.

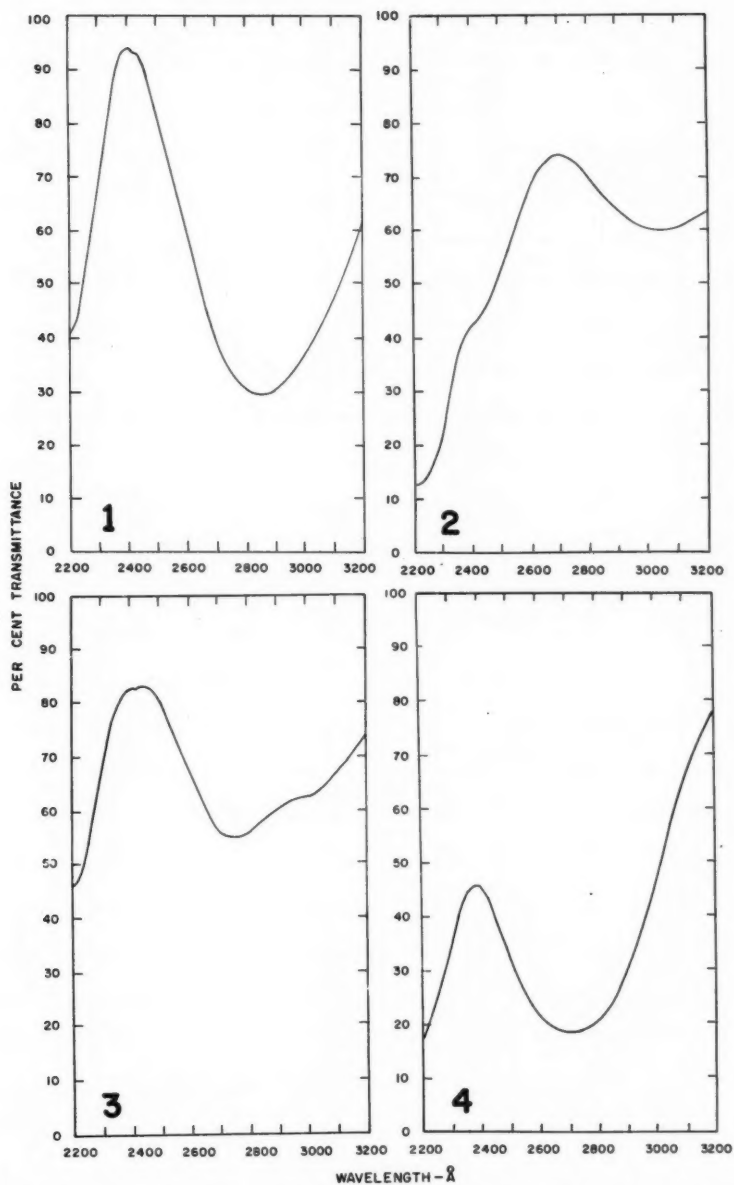


FIG. 1. Ultraviolet absorption spectrum of chlorotrihydroxydihydrophenazine.
FIG. 2. Ultraviolet absorption spectrum of chlorotrihydroxyphenazine-5,10-dioxide.
FIG. 3. Ultraviolet absorption spectrum of trichlorotrihydroxydihydrophenazine.
FIG. 4. Ultraviolet absorption spectrum of trichlorodihydroxydihydrophenazine.

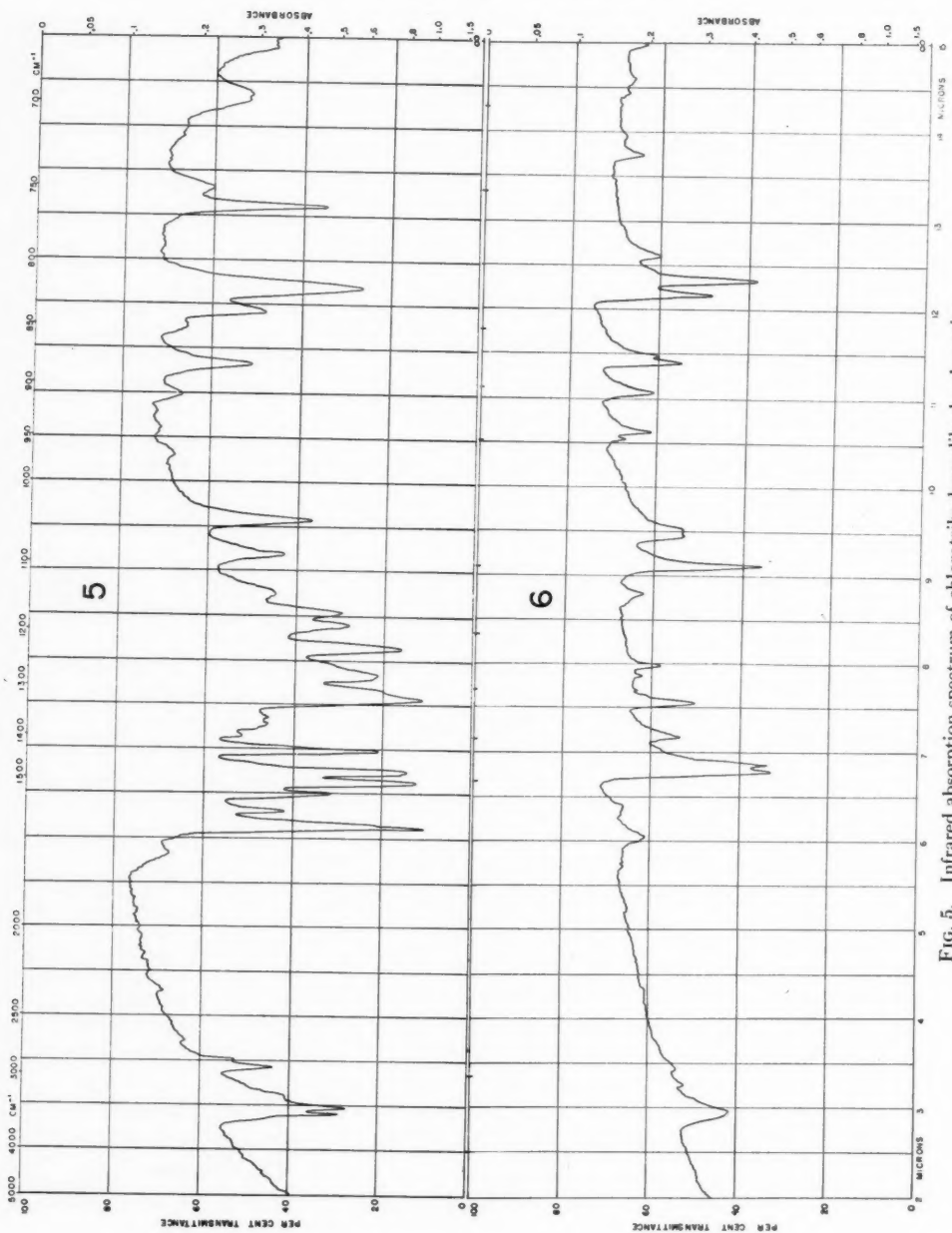


FIG. 5. Infrared absorption spectrum of chlorotrihydroxydihydrophenazine.
FIG. 6. Infrared absorption spectrum of chlorotrihydroxyphenazine-5,10-dioxide.

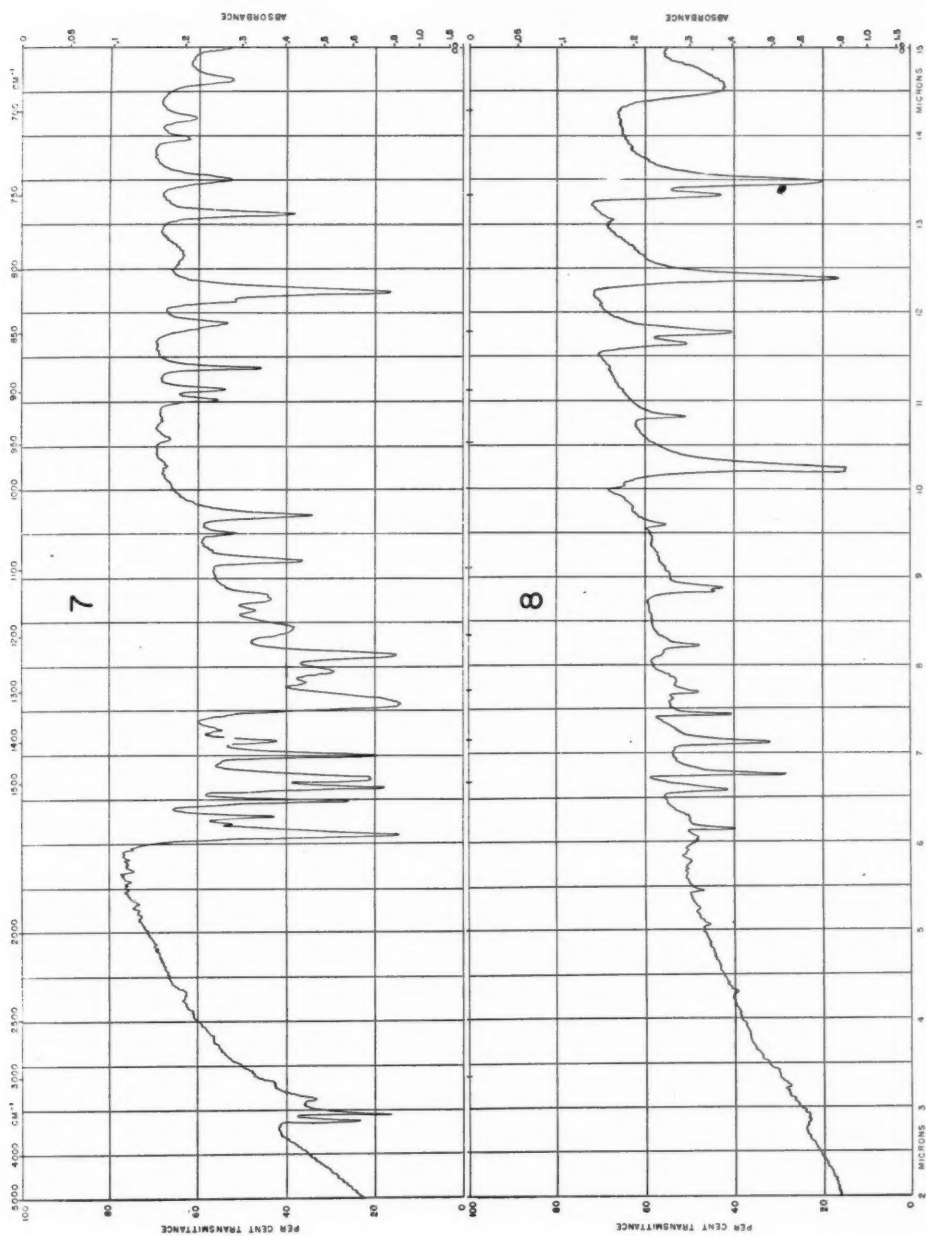


FIG. 7. Infrared absorption spectrum of bromotrihydroxydihydrophenazine.
FIG. 8. Infrared absorption spectrum of 1,6-dichlorophenazine.

EXPERIMENTAL*

*Chlorotrihydroxydihydrophenazine**Reduction*

Catalytic hydrogenation.—Chlorotrihydroxydihydrophenazine (0.2 g.) was dissolved in ethanol (80 ml.), the resulting solution placed in a thick-walled glass bottle, and 5% palladium on strontium carbonate (0.04 g.) added. The mixture was shaken with hydrogen under a pressure of 38 lb./sq. in. for 3 hours at room temperature. The catalyst was removed by filtration and the filtrate was evaporated. A pinkish-brown residue was left, which was recrystallized from ethanol as colorless plates, m.p. 185° C. Yield, 93%. The product gave a green coloration with ferric chloride solution. Calculated for $C_{12}H_{11}ON_2Cl$: C, 61.50%; H, 4.70%. Found: C, 61.00%; H, 5.00%.

Sodium hyposulphite.—Chlorotrihydroxydihydrophenazine (0.3 g.), dissolved in 20% sodium hydroxide solution, was treated with powdered sodium hyposulphite and a product was obtained which recrystallized from ethanol as colorless plates, m.p. 185° C. Yield, 40%. Calculated for $C_{12}H_{11}ON_2Cl$: C, 61.50%; H, 4.70%; N, 12.00%; Cl, 15.20%. Found: C, 61.30%; H, 4.80%; N, 11.80%; Cl, 15.10%.

Oxidation

Oxidation with sodium perborate.—Sodium perborate (0.2 g.) was dissolved in glacial acetic acid (7 ml.). Chlorotrihydroxydihydrophenazine (0.5 g.) dissolved in glacial acetic acid (5 ml.) was slowly added. The mixture was kept at 40–50° C. until reaction was complete. It was allowed to cool to room temperature. Crystals of product separated out, and were filtered off, thoroughly washed with cold water, and recrystallized from ethanol as yellow needles, m.p. 179–180° C. Yield, 75%. The product was chlorotrihydroxyphenazine-5,10-dioxide. It was sparingly soluble in glacial acetic acid and ethanol, and insoluble in water. A small quantity in 50% aqueous acetic acid (0.5 ml.) and 10% aqueous potassium iodide solution (0.25 ml.) was heated to 100° C. for 5 minutes. The solution was diluted with water (5 ml.) and starch solution added. An intense blue coloration appeared indicating the presence of an N-oxide. Calculated for $C_{12}H_7O_5N_2Cl$: C, 48.91%; H, 2.40%; N, 9.51%; Cl, 12.03%. Found: C, 49.01%; H, 2.50%; N, 9.33%; Cl, 12.06%.

Decomposition.—By refluxing in acetic anhydride for 24 hours and cooling, a product separated out; it was washed with water and recrystallized from ethanol and benzene as yellow plates, m.p. 270–271° C. Calculated for $C_{14}H_9O_4N_2Cl$: C, 55.18%; H, 2.98%; N, 9.19%. Found: C, 54.90%; H, 3.15%; N, 9.01%.

Peracetic acid oxidation.—Chlorotrihydroxydihydrophenazine (2.0 g.) in glacial acetic acid (100 ml.) and 30% hydrogen peroxide (10 ml.) was heated at 50° C. for 16 hours. The solution was diluted with an equal volume of hot water. On cooling, a bright yellow product separated, which was washed thoroughly with water and recrystallized from ethanol as yellow plates, m.p. 180° C. Yield, 95%. Calculated for $C_{12}H_7O_5N_2Cl$: C, 48.91%; H, 2.40%; N, 9.51%; Cl, 12.03%. Found: C, 48.8%; H, 2.52%; N, 9.38%; Cl, 12.30%.

Acetylation.—With acetic anhydride and sodium acetate, a monoacetyl derivative, recrystallized from ethanol as colorless plates, m.p. 126.5–127.5° C., was prepared. Calculated for $C_{14}H_9O_4N_2Cl$: C, 50.09%; H, 2.70%; N, 8.35%; Cl, 10.57%. Found: C, 50.16%; H, 2.81%; N, 8.70%; Cl, 10.68%.

*All melting points are uncorrected.

Methylation

Chlorotrihydroxydihydrophenazine, when treated with dimethyl sulphate in sodium hydroxide, gave a dimethyl derivative which was recrystallized from ethanol as yellow plates, m.p. 172–173° C. Calculated for $C_{14}H_{13}O_3N_2Cl$: C, 57.44%; H, 4.47%. Found: C, 57.10%; H, 4.33%.

Acetylation

Chlorotrihydroxydihydrophenazine (0.5 g.) was dissolved in anhydrous pyridine (5 ml.), and acetic anhydride (2 g.) was added with shaking. After the initial reaction, the solution was refluxed for 5 minutes, cooled, and poured into water (50 ml.). The product was removed by filtration, washed with cold 2% hydrochloric acid and water, and recrystallized from ethanol as colorless plates. Fractional crystallization showed that three substances were obtained, namely: mono-, di-, and tri-acetyl derivatives. The monoacetyl derivative crystallized as colorless plates, m.p. 177–178° C. Calculated for $C_{14}H_{11}O_4N_2Cl$: C, 54.82%; H, 3.62%; N, 9.15%; Cl, 11.56%. Found: C, 55.00%; H, 3.77%; N, 10.30%; Cl, 11.81%. The diacetyl derivative was obtained as colorless plates, m.p. 209–210° C. Calculated for $C_{16}H_{13}O_5N_2Cl$: C, 55.10%; H, 3.75%; N, 8.03%; Cl, 10.17%. Found: C, 55.53%; H, 3.93%; N, 8.30%; Cl, 10.33%. The triacetyl derivative crystallized as colorless plates, m.p. 164–165° C. Calculated for $C_{18}H_{15}O_6N_2Cl$: C, 55.26%; H, 3.87%; N, 7.17%. Found: C, 55.40%; H, 4.00%; N, 7.17%.

Benzoylation

Treatment of chlorotrihydroxydihydrophenazine, dissolved in anhydrous pyridine, with benzoyl chloride gave a tetrabenzoyl derivative, recrystallized from ethanol as colorless plates, m.p. 121–122° C. Calculated for $C_{40}H_{28}O_7N_2Cl$: C, 70.53%; H, 3.70%; Cl, 5.21%. Found: C, 70.47%; H, 3.62%; Cl, 4.85%.

Salts

Chlorotrihydroxydihydrophenazine was treated with dry hydrogen chloride in benzene, and a yellow product, removed by filtration, was recrystallized from aqueous ethanol as yellow needles of the hydrochloride, m.p. 200° C. Calculated for $C_{12}H_{10}O_3N_2Cl_2 \cdot HCl$: HCl, 1.00%. Found: HCl, 1.08% (potentiometric titration).

Chlorotrihydroxydihydrophenazine also formed a sulphate, which recrystallized from ethanol as yellow needles, m.p. 126–127° C. Calculated for $C_{12}H_9O_3N_2Cl \cdot H_2SO_4$: S, 8.84%. Found: S, 8.60%. Other salts formed were a perchlorate, pale yellow plates, m.p. 117–118° C. Calculated for $C_{12}H_9O_3N_2Cl \cdot HClO_4$: N, 7.67%. Found: N, 7.92%; and a picrate, pale yellow needles, m.p. 146–147° C. Calculated for $C_{18}H_{12}O_{10}N_8Cl$: C, 43.78%; H, 2.45%. Found: C, 43.95%; H, 2.50%.

Bromination

Chlorotrihydroxydihydrophenazine (0.3 g.) was dissolved in carbon tetrachloride (10 ml.), and a 5% solution of bromine in carbon tetrachloride was added until the color of bromine persisted on standing. After a few minutes, a deep yellow product separated out and was filtered off. It was recrystallized from ethanol, as reddish-brown plates, m.p. 197–198° C. Yield, 73%. The product was a monobromo compound. Calculated for $C_{12}H_8O_3N_2ClBr$: C, 41.94%; H, 2.35%; N, 8.16%. Found: C, 42.20%; H, 2.48%; N, 8.31%.

Nitrosation

Chlorotrihydroxydihydrophenazine (0.1 g.) was dissolved in dilute sulphuric acid (200 ml.) and treated with sodium nitrite (0.1 g.). After a few minutes, an excess of urea

was added. The product was extracted with ether, the solvent removed, and a yellowish-brown residue obtained, which was recrystallized from ethanol as yellow plates, m.p. 141°C . Yield, 65%. The product was the mononitroso derivative. Calculated for $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_2\text{Cl}$: N, 14.31%. Found: N, 14.06%.

Nitration

Chlorotrihydroxydihydrophenazine (0.3 g.) was gradually added to a mixture of equal volumes of concentrated nitric and sulphuric acids; the temperature was kept below 25°C . by cooling with cold water. The mixture was shaken until the reaction appeared to be complete, and then warmed gently for a few minutes, the temperature never being allowed to exceed 40°C . The mixture was poured into cold water (50 ml.) and a dark colored precipitate obtained. The product was filtered off and recrystallized from ethanol as reddish-brown plates, m.p. $75\text{--}76^{\circ}\text{C}$. Yield, 62%. The nitro derivative gave a positive test for the presence of an N-oxide. Calculated for $\text{C}_{12}\text{H}_8\text{O}_5\text{N}_3\text{Cl}$: N, 13.57%. Found: N, 13.85%.

Degradation to Phenazine

Zinc dust distillation.—Chlorotrihydroxydihydrophenazine (0.5 g.) was ground with zinc dust (3–4 g.) and the mixture poured into a pyrex test tube and covered with an equal volume of zinc dust. The zinc dust was heated first, then the mixture of zinc dust and the compound were heated to a dull red heat. A pale yellow product was obtained as a sublimate (0.05 g.) on the cooler part of the test tube. It was recrystallized from petroleum ether as yellow needles, m.p. 171°C .

Thermal decomposition.—Chlorotrihydroxydihydrophenazine (0.1 g.) was heated to 180°C .; decomposition occurred and a pale yellow sublimate (0.01 g.) formed. The product was recrystallized from petroleum ether as yellow needles, m.p. 171°C ., alone or mixed with the substance mentioned above, or with authentic phenazine.

Trichlorotrihydroxydihydrophenazine

Methylation

A monomethyl derivative, recrystallized from aqueous ethanol as orange plates, m.p. $118\text{--}119^{\circ}\text{C}$., was obtained. Calculated for $\text{C}_{13}\text{H}_9\text{O}_3\text{N}_2\text{Cl}_3$: C, 44.92%; H, 2.61%; N, 8.06%; Cl, 30.60%. Found: C, 44.97%; H, 2.55%; N, 8.19%; Cl, 30.77%.

Acetylation

With glacial acetic acid and acetic anhydride, a diacetyl derivative, recrystallized from ethanol as colorless plates, m.p. $201\text{--}202^{\circ}\text{C}$., was obtained. Calculated for $\text{C}_{16}\text{H}_{11}\text{O}_5\text{N}_2\text{Cl}_3$: C, 46.10%; H, 2.64%; N, 6.71%; Cl, 25.47%. Found: C, 46.20%; H, 2.81%; N, 6.88%; Cl, 25.70%.

Degradation to Phenazine

Zinc dust distillation and thermal decomposition of trichlorotrihydroxydihydrophenazine yielded phenazine, m.p. 171°C ., alone or mixed with authentic phenazine.

Trichlorodihydroxydihydrophenazine

Methylation

A dimethyl derivative, recrystallized from ethanol as colorless plates, m.p. $97\text{--}98^{\circ}\text{C}$., was prepared. Yield, 40%. Calculated for $\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}_3$: C, 48.65%; H, 3.21%. Found: C, 48.30%; H, 3.10%.

Acetylation

With acetic anhydride and sodium acetate, a monoacetyl derivative was obtained as colorless plates, m.p. 101°C . Calculated for $\text{C}_{14}\text{H}_9\text{O}_3\text{N}_2\text{Cl}_3$: C, 46.76%; H, 2.52%;

N, 7.80%; Cl, 29.57%. Found: C, 46.87%; H, 2.58%; N, 8.14%; Cl, 29.43%.

Degradation to Phenazine

Zinc dust distillation and thermal decomposition gave rise to phenazine, identified by mixed melting point and infrared absorption spectrum.

Bromotrihydroxydihydrophenazine

Acetylation

A monoacetyl derivative, m.p. 158–159° C., was prepared. Calculated for $C_{14}H_{11}O_4N_2Br$: C, 47.88%; H, 3.15%. Found: C, 48.00%; H, 3.38%.

Degradation to phenazine

Zinc dust distillation and thermal decomposition gave phenazine, m.p. 171° C., alone or with an authentic sample.

Molecular Weights and Absorption Spectra

Molecular Weights

The molecular weights were determined, firstly by the Rast method, and later more accurately by the ebullioscopy method. For the latter method, absolute ethanol was the solvent and a differential thermometer was used. The results obtained are shown in Table I.

TABLE I
MOLECULAR WEIGHTS

Formula	Calculated	Rast	Ebullioscopy
$C_{12}H_9O_3N_2Cl$	249	242, 233, 259	247, 246, 255
$C_{12}H_7O_3N_2Cl$	279	292, 288, 306	273, 278, 268
$C_{14}H_9O_4N_2Cl$	337	360, 349	332, 328
$C_{12}H_7O_3N_2Cl_2$	334	348, 309, 286	336, 340
$C_{12}H_7O_2N_2Cl_2$	318	296, 323, 334	318, 324

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were taken on a Beckman Spectrophotometer Model DK-2, using a hydrogen discharge tube as a light source. Stoppered quartz cells of 1.000 ± 0.002 cm. length were used for all measurements. Readings were taken using absolute ethanol as the neutral medium. Measurements were made in the spectral range 220 to 340 $m\mu$. Some of the results are shown in Figs. 1 to 4.

Infrared Absorption Spectra

The infrared absorption spectra were obtained with a Perkin-Elmer Model 21 double-beam null principle recording spectrometer.

A few of the compounds were mulled in Nujol in an agate mortar until a uniform paste was obtained. The mulled samples were placed between two freshly polished rock salt plates and spread out into a uniform film by applying pressure.

The other phenazine compounds were mulled with potassium chloride previously ground to pass through a 300 mesh sieve. Carbon tetrachloride was added and the mixture stirred. The solvent was removed with a stream of dry air to give a dispersed mixture, which was placed in a Perkin-Elmer die (13 mm. in diameter) and pressed to form a pellet (Bedard, A. M. and Meyers, J. L. Spectroscopy Symposium, C.I.C. 1955).

Infrared absorption spectra were then determined over the whole range of the spectrum from 5000 to 650 cm^{-1} ; a given slit width was used for every wavelength and these slit widths were the same for each compound.

TABLE II
INFRARED ABSORPTION MAXIMA OF PHENAZINES, CM.⁻¹

Phenazine	1660	1515	1470	1430	1360	1210
Phenazine-5,10-dioxide	1615	1576	1470	1433	1407	1357
1,6-Dichlorophenazine	1625	1518	1479	1405	1342	1214
Chlorotrihydroxydihydrophenazine	3430	3370	2910	2835	1540	1510
Chlorotrihydroxyphenazine-5,10-dioxide	3390	1650	1584	1430	1400	1320
Triacetyl derivative of chlorotrihydroxydihydrophenazine	2910	2840	1780	1730	1580	1475
Reduction product of chlorotrihydroxydihydrophenazine	3400	3320	1630	1600	1561	1467
Bromo derivative of chlorotrihydroxydihydrophenazine	3460	3380	1640	1588	1559	1547
Bromotrihydroxydihydrophenazine	3470	3380	1640	1588	1540	1505
Trichlorotrihydroxydihydrophenazine	3380	2840	1589	1542	1528	1463
Trichlorodihydroxydihydrophenazine	4260	2920	2860	1580	1504	1460
Monoacetyl derivative of trichlorodihydroxydihydrophenazine	2910	1790	1694	1639	1540	1510
Phenazine	1150	1120	1110	998	905	859
Phenazine-5,10-dioxide	1120	1096	1015	962	858	822
1,6-Dichlorophenazine	1125	1042	978	924	859	820
Chlorotrihydroxydihydrophenazine	1188	1169	1088	1046	884	838
Chlorotrihydroxyphenazine-5,10-dioxide	1138	1098	1055	1049	942	904
Triacetyl derivative of chlorotrihydroxydihydrophenazine	1186	1090	1047	1020	923	908
Reduction product of chlorotrihydroxydihydrophenazine	1195	1155	1044	1044	930	868
Bromo derivative of chlorotrihydroxydihydrophenazine	1183	1147	1090	1063	922	873
Bromotrihydroxydihydrophenazine	1187	1140	1088	1052	907	879
Trichlorotrihydroxydihydrophenazine	1157	1094	1050	1044	903	885
Trichlorodihydroxydihydrophenazine	1097	1053	1011	967	948	900
Monoacetyl derivative of trichlorodihydroxydihydrophenazine	1195	1160	1097	1041	985	922
Phenazine	1310	1375	1348	1308	1278	1258
Phenazine-5,10-dioxide	1310	1375	1348	1308	1278	1258
1,6-Dichlorophenazine	1310	1375	1348	1308	1278	1258
Chlorotrihydroxydihydrophenazine	1310	1375	1348	1308	1278	1258
Chlorotrihydroxyphenazine-5,10-dioxide	1310	1375	1348	1308	1278	1258
Triacetyl derivative of chlorotrihydroxydihydrophenazine	1310	1375	1348	1308	1278	1258
Reduction product of chlorotrihydroxydihydrophenazine	1310	1375	1348	1308	1278	1258
Bromo derivative of chlorotrihydroxydihydrophenazine	1310	1375	1348	1308	1278	1258
Bromotrihydroxydihydrophenazine	1310	1375	1348	1308	1278	1258
Trichlorotrihydroxydihydrophenazine	1310	1375	1348	1308	1278	1258
Trichlorodihydroxydihydrophenazine	1310	1375	1348	1308	1278	1258
Monoacetyl derivative of trichlorodihydroxydihydrophenazine	1310	1375	1348	1308	1278	1258

The spectrum of 1,6-dichlorophenazine, prepared by the condensation of 2-chloroaniline and 2-chloronitrobenzene, was determined for comparison. The results obtained are shown in Table II and Figs. 5 to 8.

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THE NORMAL C₁₇ FATTY ACIDS OF MUSK-OX FAT¹

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ABSTRACT

A sample of body fat of the Canadian musk ox (*Ovibos moschatus* subsp.) was converted to methyl esters and distilled. The fraction containing esters of C₁₇ acids was crystallized fractionally at low temperature and two straight-chain C₁₇ acids were isolated. *n*-Heptadecanoic acid was identified by analysis, by mixed melting point of the acid and two derivatives with authentic samples, and by its X-ray diffraction pattern. 9-Heptadecenoic acid was identified by analysis, by mixed melting point of two derivatives with authentic samples, and by oxidative cleavage. It is estimated that the fat contained 1.7% of *n*-heptadecanoic acid and 0.9% of *cis*-9-heptadecenoic acid, based on the total fatty acids. Although there was an appreciable content of *trans* acids in the fat, the heptadecenoic acid was found to contain little or none of the *trans* form.

The body fat of ruminant animals has ordinarily a rather high content of stearic acid and a low content of polyenoic acids in its glycerides, in comparison with the fat of non-ruminants. It was of interest to examine the fat of the Canadian musk ox (*Ovibos moschatus* subsp.) in order to determine whether it resembles other ruminants in this respect. The musk ox is a unique species, living in an Arctic environment, and it was thought that the body fat composition might exhibit some unusual features related to the rigorous living conditions.

It became evident in the early part of the work that the fat contained an appreciable amount of C₁₇ fatty acid or acids, and attention was concentrated on this portion of the material. The total composition of the fatty acids will be reported in a subsequent paper.

EXPERIMENTAL

A quantity of the back fat of a female adult musk ox was supplied by J. S. Tener, Canadian Wildlife Service, Department of Northern Affairs and National Resources. The animal had been taken in its natural habitat in Northern Canada and was described as healthy and well-nourished.

A portion of the fat was immersed in 10% aqueous potassium hydroxide solution and heated on the steam bath under nitrogen until dissolution was complete. The mixture was acidified while warm with hydrochloric acid and the fatty acids which solidified on cooling were removed. The remaining liquor was extracted with ether to recover traces of fatty acids and the extract was combined with the main portion.

The total fatty acids were esterified by boiling with methanol containing 2% of dry hydrogen chloride. In this procedure, any unsaponified glyceride is also converted to methyl ester. The esters were washed and dried in the ordinary way.

The mixed esters, weight 300 g., iodine value 39.5, were distilled through a Podbielniak Heli-grid column at a pressure of 0.5 mm. An inflection in the distillation curve between the usual C₁₆ and C₁₈ sections was evidence of acid(s) of chain length C₁₇ (Fig. 1, curve A).

Fractions 4, 5, and 6 (Table I), which were judged to contain all or nearly all of the esters of C₁₇ acids, were combined. This material, 15.3 g., iodine value 29.9, was redistilled through a spinning band column, also at 0.5 mm. pressure. It yielded a relatively large fraction disilling mainly at 131° at 0.5 mm. (Fig. 1, curve B).

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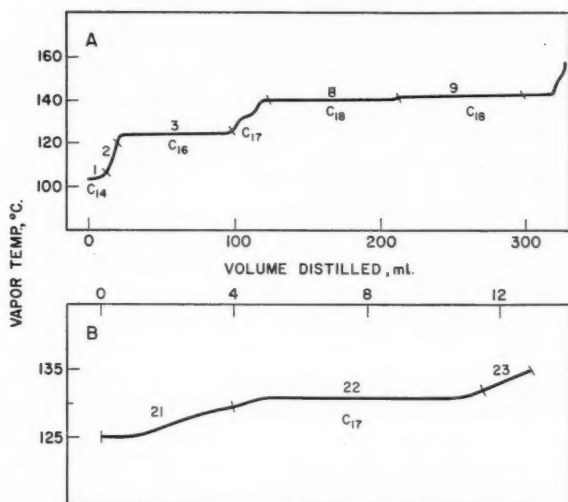


FIG. 1. Distillation of the methyl esters of musk-ox fat. A, main distillation curve showing the C_{17} portion. B, redistillation of combined fractions, 4, 5, and 6, which contain the C_{17} portion. Fraction numbers are shown above the curves.

TABLE I
DISTILLATION OF METHYL ESTERS

Fraction	Temp., ° C. (0.5 mm.)	Weight, g.	Chain length	Iodine value
3	123-125	68.5	C_{16}	8.0
4	125-129	2.3		
5	129-132	5.4		
6	132-139	7.6		
7	139-140	6.5	C_{18}	86.1
8	140-141	76.9	C_{18}	90.5

TABLE II
REDISTILLATION OF C_{17} ESTERS

Fraction	Temp., ° C. (0.5 mm.)	Weight, g.	Iodine value
21	125-130	3.3	11.7
22	130-133	7.0	21.5
23	133-137	1.3	33.4
2R		2.7	73.5

This portion of the methyl esters, fraction 22 (Table II), was recrystallized from 70 ml. of acetone, giving the following fractions:

Fraction	Temp. of crystn., ° C.	Yield, g.
221	-20	2.2 (solid)
222	-50	2.2 (liquid)
223	Filtrate	1.3 (liquid)

Heptadecanoic Acid

Fraction 221 was saponified and the acid was recrystallized from ethanol, yielding heptadecanoic acid, m.p. 61.0–61.5°.* The reported m.p. is 61.1–61.3° (8). When mixed with synthetic heptadecanoic acid melting at 60.5–61° (Eastman Kodak Co.; made from cetyl bromide via cetyl cyanide), the mixture melted at 60.5–61°. The equivalent weight of the natural acid by titration was 270.2, 270.7 (theory 270.4). Calc. for $C_{17}H_{34}O_2$: C, 75.51; H, 12.67; CH_3 groups, 1. Found: C, 75.70; H, 12.64; CH_3 groups, 0.87.

The X-ray diffraction pattern was determined in comparison with that of the synthetic heptadecanoic acid by Dr. M. Przybylska of these laboratories, who reported that the patterns were indistinguishable and confirmed that the two substances were identical. The X-ray patterns were obtained with copper radiation and a Debye-Scherrer camera.

Methyl heptadecanoate, made from musk-ox fat, was treated with hydroxylamine hydrochloride, giving heptadecanoic N-hydroxyamide. After recrystallizing twice from acetic acid and once from ether it melted at 103.5–104°, alone and mixed with a synthetic sample. Calc. for $C_{17}H_{35}O_2N$: N, 4.91. Found: N, 4.93. This substance has not been recorded previously.

p-Phenylphenacyl heptadecanoate was prepared and recrystallized from ethanol. It melted at 94.5–95°, alone and mixed with a synthetic sample.

9-Heptadecenoic Acid

Fraction 223 was saponified and the acid was recrystallized from 13 ml. of acetone at –50°, yielding 0.73 g. of heptadecenoic acid, m.p. 9–10°. The reported melting point of synthetic *cis*-9-heptadecenoic acid is 13.0–13.5° (1). Calc. for $C_{17}H_{32}O_2$: C, 76.07; H, 12.01; equivalent weight, 268.4. Found: C, 75.84; H, 12.24; equivalent weight 269.5.

A portion was hydrogenated in methanol with Adams' catalyst, giving heptadecanoic acid, m.p. 60.5–61°, alone and mixed with synthetic heptadecanoic acid, m.p. 60.5–61°.

Hydroxylation of the acid by alkaline permanganate gave an acid which melted at 127–128° after successive recrystallizations from ethanol and from ethyl acetate. When mixed with authentic *erythro*-9,10-dihydroxyheptadecanoic acid, m.p. 127–128°, kindly supplied by Drs. D. E. Ames and R. E. Bowman, the melting point was unchanged.

Cleavage of the heptadecenoic acid from musk-ox fat by the periodate–permanganate method (5), followed by elimination of the monobasic acid fragment by steam distillation, gave azelaic acid, m.p. 105–106°, alone and mixed with authentic azelaic acid, m.p. 105–106°. The original acid is therefore 9-heptadecenoic acid.

Its infrared absorption spectrum showed no peak or shoulder at 965 cm^{-1} . The specific absorption coefficient at this wavelength was 0.13 or almost the same as that of oleic acid. Taking into account the probable error of the method, it is judged that at least 95% of the heptadecenoic acid was of the *cis* form.

It is estimated from the weight and constants of the respective fractions and the amounts of pure acid isolated that the total fatty acids contain 1.7% of heptadecanoic acid and 0.9% of 9-heptadecenoic acid.

The diene content of the C_{17} fraction, determined by ultraviolet absorption after alkali isomerization, was negligible.

DISCUSSION

The heptadecanoic acid isolated from musk-ox fat cannot be an equimolecular mixture of palmitic and stearic acids because, as has been pointed out previously (2), such a

*Melting points were determined with short stem Anschütz thermometers and are uncorrected.

mixture melts not higher than 57°. Further, the X-ray pattern of such a mixture would be quite different from that of heptadecanoic acid. Identification as heptadecanoic acid was confirmed by the preparation of pure chemical derivatives. The identification of 9-heptadecenoic acid is likewise unequivocal.

Occurrence of these acids in the fat of the musk ox is not unexpected in view of the work of Shorland and his colleagues, who were the first to establish the presence of long-chain odd-numbered carbon fatty acids in the body fat of ruminants on normal diets. Heptadecanoic acid was found by them in mutton fat (3) and 9-heptadecenoic acid in lamb caul fat (6).

The amounts of normal C₁₇ acids in musk-ox fat are apparently larger than in the fat of the sheep. Our estimate of 1.7% heptadecanoic acid and 0.9% of 9-heptadecenoic acid in the fatty acids from musk ox compares with the estimates of 1.2% and a trace, respectively, in the fatty acids from sheep fat (7).

It is unlikely that the C₁₇ fatty acids are obtained directly from the fat of the diet. The formation of odd-numbered carbon fatty acids by ruminants is believed to occur by condensation of acetate and propionate units in the metabolic process (4). Possibly some factor in the metabolism of the musk ox favors the production of these acids to a somewhat greater extent than in other animals. The fact that the heptadecenoic acid was in the *cis* form suggests that the synthesis in the animal organism is similar to the synthesis of oleic acid from acetate units.

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PREPARATION AND CHEMISTRY OF Δ^8 -HEXAHYDRO-1,4,8-PYRIMIDAZOLE, Δ^9 -1,5,9-TRIAZABICYCLO(4.4.0)DECENE, AND Δ^9 -1,4,9-TRIAZABICYCLO(5.3.0)DECENE¹

A. F. MCKAY AND M.-E. KRELING

ABSTRACT

The preparations of Δ^8 -hexahydro-1,4,8-pyrimidazole, Δ^9 -1,5,9-triazabicyclo(4.4.0)decene, and Δ^9 -1,4,9-triazabicyclo(5.3.0)decene from the corresponding 2-(ω -hydroxyalkylamino)- Δ^2 -1,3-diazacycloalkenes by chlorination and dehydrohalogenation are described. The nitro derivatives of these bicyclic compounds are more stable towards refluxing ethanol than 1-nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole.

The guanidino bicyclic compounds Δ^8 -hexahydro-1,4,8-pyrimidazole (III, $n = 3$, $m = 2$), Δ^9 -1,5,9-triazabicyclo(4.4.0)decene (III, n and $m = 3$), and Δ^9 -1,4,9-triazabicyclo(5.3.0)decene (III, $n = 4$, $m = 2$) were prepared by the general method which was previously employed in the synthesis of 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole (5) and its derivatives (3).

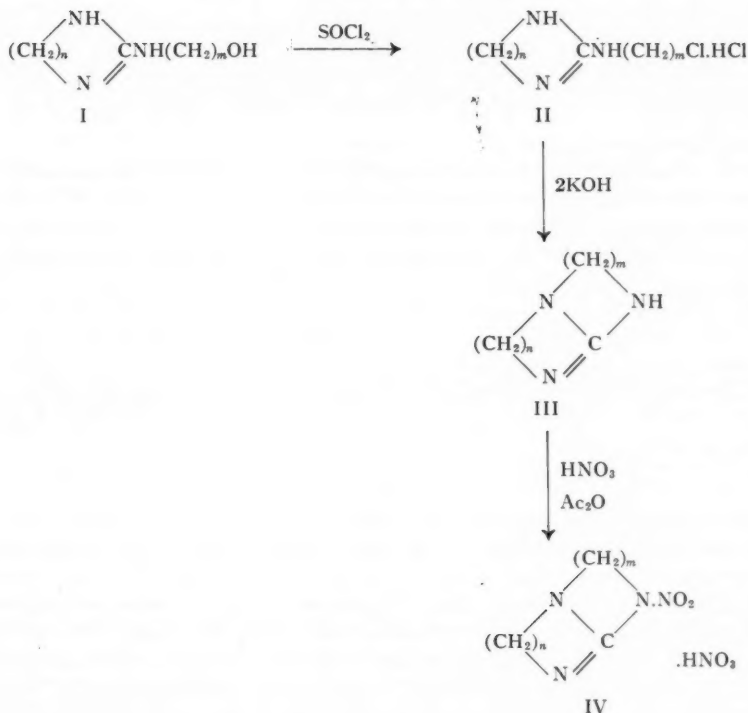
The 2-(ω -hydroxyalkylamino)- Δ^2 -1,3-diazacycloalkenes (I) were prepared in excellent yields by refluxing the alkanolamines with 2-methylmercapto- Δ^2 -1,3-diazacycloalkene salts. This is the same process used by Aspinall and Bianco (1) in the preparation of 2-alkylamino- Δ^2 -imidazolinium iodides from amines and 2-methylmercapto-2-imidazolinium iodide. These 2-(ω -hydroxyalkylamino)- Δ^2 -1,3-diazacycloalkenes (I) on chlorination with thionyl chloride gave the corresponding 2-(ω -chloroalkylamino)- Δ^2 -1,3-diazacycloalkene hydrochlorides (II) in good yields. The latter compounds on dehydrohalogenation with boiling methanolic potassium hydroxide solution gave the corresponding bicyclic compounds III in yields varying between 25.6% and 69.9%.

The same bicyclic product was obtained from 2-(β -hydroxyethylamino)- Δ^2 -tetrahydropyrimidine (I, $n = 3$, $m = 2$) and 2-(γ -hydroxypropylamino)- Δ^2 -imidazoline (I, $n = 2$, $m = 3$). Thus the double bond in the final bicyclic guanidino compound must be in the ring with least strain. At present this bicyclic compound has been assigned structure III ($n = 3$, $m = 2$). Δ^8 -Hexahydro-1,4,8-pyrimidazole (III, $n = 3$, $m = 2$) on nitration in nitric acid-acetic anhydride medium gives only one nitration product. The nitration product (m.p. 145.5–146° C.) gave analytical values in agreement with those calculated for 1-nitro- Δ^8 -hexahydro-1,4,8-pyrimidazole nitrate (IV, $n = 3$, $m = 2$). This nitro compound was recovered unchanged after it had been refluxed in absolute ethanol for 2½ hours. Thus 1-nitro- Δ^8 -hexahydro-1,4,8-pyrimidazole nitrate is much more stable than 1-nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole nitrate (5). The latter compound on being refluxed in absolute ethanol was converted into 1-(β -nitraminoethyl)-2-imidazolidone.

The symmetrical bicyclic guanidino compound, Δ^9 -1,5,9-triazabicyclo(4.4.0)decene (III, m and $n = 3$), was prepared from 2-(γ -hydroxypropylamino)- Δ^2 -tetrahydropyrimidine (I, m and $n = 3$). This bicyclic containing the two 6-membered rings formed a carbonate very readily. It was much more difficult to obtain in a pure state and it was identified as its picrate (m.p. 220.5–222° C.). This difficulty with carbonate formation was not encountered with the 5,5-, 5,6-, and 5,7-membered bicyclic guanidino compounds.

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Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Limited, Ville LaSalle, Quebec.



Δ^1 , Δ^5 , Δ^9 -Triazabicyclo(4.4.0)decene on nitration gave a 49% yield of 1-nitro- Δ^1 , Δ^5 , Δ^9 -triazabicyclo(4.4.0)decene nitrate (m.p. 100–101° C.). This nitro derivative IV (m and $n = 3$) was recovered unchanged after it had been refluxed for 2½ hours in absolute ethanol.

The 5,7-membered bicyclo guanidino compound was obtained from 2-(β -hydroxyethylamino)- Δ^2 -1,3-diazacycloheptene (I, $n = 4$, $m = 2$) in relatively good yields. This compound could exist as structure III with $n = 4$ and $m = 2$ or $n = 2$ and $m = 4$. At present the former structure is preferred but it has not been proved. The 5,7-membered bicyclic guanidino compound on nitration gives a mono nitro derivative in quantitative yield which on the basis of structure III ($n = 4$, $m = 2$) would be 1-nitro- Δ^1 , Δ^4 , Δ^9 -triazabicyclo(5.3.0)decene nitrate (IV, $n = 4$, $m = 2$).

EXPERIMENTAL²

2-Methylmercapto-2-imidazolinium Iodide

2-Methylmercapto-2-imidazolinium iodide (m.p. 141–143° C.) was prepared in 92% yield by the method of Aspinall and Bianco (1).

Hexahydropyrimidine-2-thione

Hexahydropyrimidine-2-thione (m.p. 212–212.5° C.) was prepared in 67.5% yield as previously described (4).

²All melting points are uncorrected. The microanalyses were determined by Micro Tech Laboratories, Skokie, Illinois.

2-Methylmercapto- Δ^2 -tetrahydropyrimidinium Iodide

Methylation of hexahydropyrimidine-2-thione as previously (4) described gave a 96.6% yield of 2-methylmercapto- Δ^2 -tetrahydropyrimidinium iodide (m.p. 146–147° C.). One crystallization from ethanol raised the melting point to 149° C.

1,3-Diazacycloheptane-2-thione

A stirred solution of 1,4-diaminobutane (88.15 g., 1 mole) in ethanol (200 cc.) was maintained below 20° C. while carbon disulphide (76.13 g., 1 mole) was added over a period of 30 minutes. The precipitate (m.p. 168–171° C.) was removed by filtration and washed with ethanol (100 cc.), yield 158.5 g. (96.5%). The reported (7) melting point of the inner salt of the dithiocarbamate of tetramethylenediamine is 173° C. The inner salt (100 g.) was refluxed in water (500 cc.) for 14 hours, during which time hydrogen sulphide was evolved. This solution on cooling deposited a mixture of crystals and oil. The crystals and oil were separated by extraction with hot water. The aqueous solution on cooling deposited crystals (m.p. 177–179° C.) of 1,3-diazacycloheptane-2-thione, yield 50.5 g. (63.2%). The melting point of tetramethylenethiourea is reported (7) in the literature as 177° C.

2-Methylmercapto- Δ^2 -1,3-diazacycloheptene Hydroiodide

Tetramethylenethiourea (34.0 g., 0.26 mole) in absolute methanol (100 cc.) was refluxed with methyl iodide (40.3 g., 0.29 mole) for 30 minutes. The solution was cooled and ether (150 cc.) was added. The crystals (m.p. 126.5–128.5° C.) were recovered by filtration, yield 68.0 g. (95.8%). Two crystallizations from methanol-ether solution raised the melting point to 127.5–128.5° C. Anal. Calc. for $C_6H_{12}IN_2S$: C, 26.47; H, 4.81; N, 10.30%. Found: C, 26.70; H, 4.95; N, 10.43%. The picrate formed in the usual manner from water melted at 158–159° C. Anal. Calc. for $C_{12}H_{16}N_6O_7S$: C, 38.61; H, 4.05; N, 18.77; S, 8.59%. Found: C, 38.66; H, 4.23; N, 18.54; S, 8.46%.

2-(γ -Hydroxypropylamino)-2-imidazolinium Iodide and Chloride

A solution of 2-methylmercapto-2-imidazolinium iodide (400 g., 1.64 moles) and 3-amino-1-propanol (123 g., 1.64 moles) in absolute ethanol (500 cc.) was refluxed until the evolution of methyl mercaptan had ceased. The oil which remained after removal of the ethanol *in vacuo* crystallized when left standing for 2 days at room temperature, yield 445 g. (100%). The melting point of the crystals was raised from 48–55° C. to 71.5–73° C. by two crystallizations from absolute methanol-ethyl acetate (1:4) solution. Anal. Calc. for $C_6H_{14}IN_3O$: C, 26.58; H, 5.21; N, 15.50; I, 46.81%. Found: C, 26.66; H, 5.07; N, 15.60; I, 46.53%.

2-(γ -Hydroxypropylamino)-2-imidazolinium iodide (435 g., 1.6 moles) in absolute methanol (8700 cc.) was passed through a column of IRA-400 resin³ at the rate of 12 cc. per minute. The resin was washed with methanol (8 l.) until no further precipitate was obtained with aqueous picric acid solution and then the eluate and washings were evaporated to dryness *in vacuo* under nitrogen. The residual oil was acidified with concentrated hydrochloric acid (140 cc.) and the solution was evaporated to dryness *in vacuo* under nitrogen, yield 294 g. A sample (3 g.) of this light yellow crystalline solid (93–95.5° C.) was crystallized from methanol-ethyl acetate (1:2) solution. The pure product melted at 95–96° C. Anal. Calc. for $C_6H_{14}ClN_3O$: C, 40.12; H, 7.85; N, 23.39; Cl, 19.74%. Found: C, 39.90; H, 7.84; N, 22.91; Cl, 19.90%.

³Exhausted IRA-400 resin (4 l.) was placed in a glass column (diam. 7 cm., height 90 cm.) and it was regenerated with 12 l. of 4% aqueous sodium hydroxide solution. The column of resin was washed with water (6 l.) and absolute methanol (5 l.).

2-(γ-Chloropropylamino)-2-imidazolinium Chloride

Purified thionyl chloride (251.0 g., 2.11 moles) was added over a period of 1 hour at room temperature to a stirred solution of 2-(γ-hydroxypropylamino)-2-imidazolinium chloride (291 g., 1.62 moles) in freshly distilled chloroform (900 cc.). After this reaction had been heated at 40° C. for 1 hour and at 60–65° C. for 3 hours, it was evaporated to dryness *in vacuo* under nitrogen, yield 319.1 g. (99.4%).

A sample (579 mg.) of this semicrystalline viscous oil on treatment with saturated aqueous picric acid solution gave a crystalline picrate (m.p. 160–163° C.), yield 1.02 g. (89.3%). Three crystallizations from water raised the melting point to 166–166.5° C. Anal. Calc. for $C_{12}H_{16}ClN_6O_7$: C, 36.88; H, 3.87; N, 21.52; Cl, 9.08%. Found: C, 37.10; H, 3.95; N, 21.58; Cl, 9.46%.

2-(β-Hydroxyethylamino)-Δ²-tetrahydropyrimidine Picrate

2-Methylmercapto-Δ²-tetrahydropyrimidinium iodide (94.5 g., 0.366 mole) and ethanolamine (22.3 g., 0.366 mole) in absolute ethanol (200 cc.) were refluxed for 3½ hours until the evolution of methyl mercaptan had subsided. The solution was evaporated to dryness *in vacuo* under nitrogen. The residue was a slightly yellow crystalline solid, yield 100 g.

The crude 2-(β-hydroxyethylamino)-Δ²-tetrahydropyrimidinium iodide (98.8 g., 0.365 mole) in water (2 l.) was passed through a column of IRA-400 resin (1 l. of resin in the hydroxyl form in a column 5 cm. in diam.) at the rate of 10 cc. per minute. The column was washed with water (6 l.) and the combined eluate and washings were concentrated to 800 cc. This solution was acidified with concentrated hydrochloric acid (28 cc.) and then evaporated to dryness *in vacuo*. The yield was 65.5 g. (100%). A sample of the semicrystalline oil gave a crystalline picrate (m.p. 119–122° C.) on treatment with saturated aqueous picric acid solution. Two crystallizations from ethanol raised the melting point to 129° C. Anal. Calc. for $C_{12}H_{16}N_6O_8$: C, 38.72; H, 4.33; N, 22.59%. Found: C, 38.77; H, 4.33; N, 22.91%.

2-(β-Chloroethylamino)-Δ²-tetrahydropyrimidinium Chloride

Purified thionyl chloride (55.9 g., 0.47 mole) was added to a stirred solution of 2-(β-hydroxyethylamino)-Δ²-tetrahydropyrimidinium chloride (65 g., 0.362 mole) in freshly distilled chloroform (200 cc.) at room temperature. After the initial reaction had subsided, the solution was refluxed for 4 hours. The solvent and excess thionyl chloride were removed *in vacuo* to yield 72 g. (100%) of dark brown oil. A sample (571 mg.) of the oil on treatment with a saturated aqueous picric acid solution gave 645 mg. (57.4%) of a crystalline picrate (m.p. 153–156° C.). Two crystallizations from water raised the melting point to 157.5–158° C. Anal. Calc. for $C_{12}H_{16}ClN_6O_7$: C, 36.89; H, 3.87; N, 21.52; Cl, 9.08%. Found: C, 36.69; H, 3.96; N, 21.90; Cl, 8.90%.

*Δ⁸-Hexahydro-1,4,8-pyrimidazole**Method A*

A solution of 2-(γ-chloropropylamino)-2-imidazolinium chloride (307 g., 1.55 moles) in absolute methanol (1 l.) was placed in a three-necked flask fitted with a stirrer, condenser, and dropping funnel. The solution was heated to reflux with stirring, and potassium hydroxide (173.9 g., 3.10 moles) in absolute methanol (1865 cc.) was added over a period of 85 minutes. After the reaction mixture had refluxed for a further 4 hours, it was allowed to cool and the precipitated potassium chloride was removed by filtration, yield 208.2 g. (90%). The filtrate was evaporated to dryness *in vacuo* under nitrogen.

The semicrystalline residue was extracted with chloroform (500 cc.) to eliminate residual potassium chloride and the chloroform solution was evaporated *in vacuo* under nitrogen. The crude product on distillation gave 132 g. (69.9%) of pale yellow crystals (b.p. 103–105° C./0.1 mm.). A sample (17.3 g.) of these crystals was crystallized from acetone at –15° C. The pure material melted at 64–65° C., yield 8.1 g. This material combined readily with carbon dioxide from the air and it was hygroscopic. Thus a picrate was prepared for analysis. The picrate prepared in the usual manner from water melted at 228.5–229° C., yield 92%. One crystallization from water raised the melting point to 230° C. Anal. Calc. for $C_{12}H_{14}N_8O_7$: C, 40.67; H, 3.98; N, 23.73%. Found: C, 40.71; H, 4.07; N, 23.63%.

Method B

2-(β -Chloroethylamino)- Δ^2 -tetrahydropyrimidinium chloride (71 g., 0.359 mole) in absolute methanol (150 cc.) was treated with 2 mole equivalents of potassium hydroxide in methanol under the conditions described above under Method A for the dehydrohalogenation of 2-(γ -chloropropylamino)-2-imidazolinium chloride. The final product was a semicrystalline brown oil, yield 45 g.

A paper chromatogram of the oil developed with butanol – water – acetic acid (4:5:1) solvent on No. 1 Whatman chromatography paper showed two spots with R_f values of 0.54 and 0.24. A sample of Δ^8 -hexahydro-1,4,8-pyrimidazole (m.p. 65° C.) from the preparation described above in Method A gave a R_f value of 0.55 ± 0.01 when its paper chromatogram was prepared under identical conditions.

An aqueous solution of oil (247 mg.) gave a crystalline picrate (m.p. 212–224° C.), yield 283 mg. (40.5%). Two crystallizations from water raised the melting point to 228.5–230° C. This picrate did not depress the melting point of Δ^8 -hexahydro-1,4,8-pyrimidazole picrate (m.p. 230° C.) prepared from 2-(γ -chloropropylamino)-2-imidazolinium chloride.

A portion (35.5 g.) of the brown oil on distillation *in vacuo* at 0.04 mm. pressure gave 9.86 g. of oil and 3.36 g. of sublimed crystals. The brown tar-like residue was discarded. The oil was redistilled *in vacuo* to give 8.4 g. of colorless oil (b.p. 112–115° C. at 0.3 mm.) which crystallized on cooling to 0° C. The melting point of this material was raised from 58–61° C. to 63–65° C. by one crystallization from acetone. A mixture melting point determination with the crystals (m.p. 64–65° C.) obtained above in Method A showed no depression.

The crystalline sublimate (3.36 g.) from the first distillation sublimed between 241° and 255° C. A sample of the sublimed crystals (40 mg.) in water (1 cc.) was treated with saturated aqueous picric acid solution. The crystalline picrate (m.p. 187–189° C.) was obtained in 81.5% (107 mg.) yield. Two crystallizations from water raised the melting point to 190–191° C. A mixture melting point determination with the picrate (2) of 1,3-diazacyclohexanone-2 showed no depression.

2-(γ -Hydroxypropylamino)- Δ^2 -tetrahydropyrimidinium Iodide and Chloride

2-(γ -Hydroxypropylamino)- Δ^2 -tetrahydropyrimidinium iodide was prepared in quantitative yield from 2-methylmercapto- Δ^2 -tetrahydropyrimidinium iodide and 3-amino-1-propanol under the conditions described above for the preparation of 2-(γ -hydroxypropylamino)-2-imidazolinium iodide.

A sample (606.6 mg.) of the oil on treatment with a saturated aqueous picric acid solution gave a 47.3% (387 mg.) yield of a crystalline picrate (m.p. 132–137° C.). Two crystallizations from water raised the melting point to 138–139° C. Anal. Calc. for

$C_{13}H_{18}N_6O_8$: C, 40.41; H, 4.69; N, 21.75%. Found: C, 40.30; H, 4.52; N, 22.00%. 2-(γ -Hydroxypropylamino)- Δ^2 -tetrahydropyrimidinium chloride was prepared in quantitative yield from the iodide salt by the method described above for the conversion of the iodide salt of 2-(γ -hydroxypropylamino)-2-imidazoline into its hydrochloride.

2-(γ -Chloropropylamino)- Δ^2 -tetrahydropyrimidinium Chloride

2-(γ -Hydroxypropylamino)- Δ^2 -tetrahydropyrimidinium chloride (47.4 g., 0.25 mole) and thionyl chloride (38.0 g., 0.32 mole) in freshly distilled chloroform (150 ml.) were refluxed for $3\frac{1}{2}$ hours. The reaction product was worked up by the method described above in the preparation of 2-(γ -chloropropylamino)-2-imidazolinium chloride to give 51 g. (98%) of a light brown oil.

A sample of this oil in water gave a crystalline picrate (m.p. 147–148.5° C.) in 53.8% yield. Three crystallizations from absolute ethanol raised the melting point to 150–151° C. Anal. Calc. for $C_{13}H_{17}ClN_6O_7$: C, 38.56; H, 4.23; Cl, 8.76; N, 20.76%. Found: C, 38.81; H, 4.44; Cl, 8.65; N, 20.56%.

Δ^9 -1,5,9-Triazabicyclo(4.4.0)decene

2-(γ -Chloropropylamino)- Δ^2 -tetrahydropyrimidinium chloride (52 g., 0.25 mole) was refluxed with two mole equivalents of potassium hydroxide in methanol (300 cc.) for 4 hours. The product was recovered as a semicrystalline solid by the same procedure used above in the preparation of Δ^8 -hexahydro-1,4,8-pyrimidazole, yield 39.0 g.

The crude reaction product gave two spots on a paper chromatogram developed with butanol–water–acetic acid (4:5:1) solution. These spots, which were developed with bromocresol green, had R_f values of 0.55 ± 0.01 and 0.24 ± 0.01 . When the pure bicyclic compound was isolated, it was found to have an R_f value of 0.55 ± 0.01 under similar conditions while 1,3-diazacyclohexanone-2 had an R_f value of 0.24.

A portion (29.3 g.) of the semicrystalline solid was extracted in a Soxhlet extractor with ethyl acetate (1×600 cc.) and then acetone (7×250 cc.). On cooling these combined solutions deposited 197 mg. of crystals which sublimed at 255° C. These crystals on treatment with aqueous picric acid solution gave a crystalline picrate (m.p. 186–188° C.). One crystallization from water raised the melting point to 190° C. This picrate on admixture with a sample of the picrate of 1,3-diazacyclohexanone-2 (m.p. 191° C.) (2) showed no depression.

The solvent from the extraction on concentration and cooling gave crystals melting at 146–175° C., yield 8.7 g. (25.6%). These crystals could not be purified because they always crystallized as a mixture of free base and its carbonate salt. A sample of the crystals on treatment with a saturated aqueous picric acid solution gave a 90.2% yield of crystalline picrate (m.p. 216–220° C.). Two crystallizations from absolute ethanol raised the melting point to 220.5–222° C. Anal. Calc. for $C_{13}H_{16}N_6O_7$: C, 42.39; H, 4.38; N, 22.82%. Found: C, 42.38; H, 4.52; N, 22.57%.

2-(β -Hydroxyethylamino)- Δ^2 -1,3-diazacycloheptene Hydrochloride

2-(β -Hydroxyethylamino)- Δ^2 -1,3-diazacycloheptene hydroiodide was prepared in quantitative yield from ethanolamine and 2-methylmercapto- Δ^2 -1,3-diazacycloheptene hydroiodide by the procedure described (5) for the preparation of 2-(β -hydroxyethylamino)-2-imidazolinium iodide.

2-(β -Hydroxyethylamino)- Δ^2 -1,3-diazacycloheptene hydroiodide (129 g., 0.453 mole) in methanol (2.6 l.) was passed through a column of IRA-400 resin (1.4 liters of resin in the hydroxyl form previously washed with methanol (6 l.)) at a rate of 30 cc. per

minute. After the column was washed with methanol (5 l.), the combined eluates (7.6 l.) were concentrated to a volume of 400 cc. under nitrogen at reduced pressure. A sample of this solution on treatment with a saturated aqueous solution of picric acid gave a crystalline picrate (m.p. 103° C.). Anal. Calc. for $C_{13}H_{18}N_6O_8$: C, 40.41; H, 4.70; N, 21.76%. Found: C, 40.37; H, 4.59; N, 21.90%. The methanolic solution of free base was acidified with concentrated hydrochloric acid solution (43 cc.) and then evaporated to dryness *in vacuo*.

2-(β-Chloroethylamino)-Δ²-1,3-diazacycloheptene Hydrochloride

A mixture of 2-(β-hydroxyethylamino)-Δ²-1,3-diazacycloheptene hydrochloride (87 g., 0.453 mole) and purified thionyl chloride (71 g., 0.6 mole) in freshly distilled chloroform (250 cc.) was refluxed for 3½ hours. The solvent and excess thionyl chloride were removed *in vacuo*. A reddish-brown colored oil remained, yield 95.5 g. (100%). A sample (280 mg.) of this oil in water (2 cc.) on treatment with a saturated aqueous picric acid solution gave 385 mg. (72%) of a crystalline picrate (m.p. 121–122° C.). Two crystallizations from methanol–water solution raised the melting point to 122.5–123° C. Anal. Calc. for $C_{13}H_{17}ClN_6O_7$: C, 38.56; H, 4.23; Cl, 8.76; N, 20.76%. Found: C, 38.62; H, 4.43; Cl, 8.97; N, 21.03%.

Δ⁹-1,4,9-Triazabicyclo(5.3.0)decene

2-(β-Chloroethylamino)-Δ²-1,3-diazacycloheptene hydrochloride (95.5 g., 0.45 mole) was dehydrohalogenated by the same procedure used in the preparation of 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole (5). A pale yellow crystalline solid containing some potassium chloride was obtained, yield 67.7 g.

A paper chromatogram of the oil on No. 1 Whatman chromatography paper using butanol–acetic acid–water (4:1:5) solvent showed one spot with an R_f value of 0.60 ± 0.02 . The spot was developed with bromocresol green indicator. The crude material (502 mg.) in water gave a crystalline picrate (m.p. 211–213° C.), yield 1.18 g. (89.7%). One crystallization from absolute methanol raised the melting point to 216–218° C. Anal. Calc. for $C_{13}H_{16}N_6O_7$: C, 42.39; H, 4.38; N, 22.82%. Found: C, 42.23; H, 4.55; N, 22.51%.

The crude product was crystallized from acetone (250 cc.) to give 27 g. of crystalline product melting at 107–111° C. After the mother liquors were concentrated to 150 cc. a second crop (6 g.) of crystals (m.p. 106–111° C.) was obtained. The mother liquors from the second crop on evaporation *in vacuo* under nitrogen gave an oil which was distilled. A colorless oil (b.p. 118–122° C. at 0.26 mm.) was obtained and it crystallized almost immediately, yield 6.5 g. The total yield of Δ⁹-1,4,9-triazabicyclo(5.3.0)decene was 39.5 g. (63.1%). A sample (1.1 g.) of these crystals (m.p. 107–111° C.) was purified for analysis by crystallization from acetone. The final melting point was 109–111° C. Anal. Calc. for $C_7H_{13}N_3$: C, 60.40; H, 9.41; N, 30.19%. Found: C, 60.24; H, 9.37; N, 29.81%.

1-Nitro-Δ⁹-1,5,9-triazabicyclo(4.4.0)decene Nitrate

Δ⁹-1,5,9-Triazabicyclo(4.4.0)decene (1.5 g., 0.010 mole) was added over a period of 20 minutes to a solution of absolute nitric acid (4.98 cc., 0.11 mole) in acetic anhydride (10.2 cc., 0.10 mole) at 0° C. The temperature was allowed to rise to 32° C. over a period of 5 minutes and it was held at this temperature for 20 minutes. This solution was poured into 150 cc. of cold ether. The ether supernatant was decanted from the oil and the oil was washed with ether several times by decantation, the oil was dissolved in absolute

ethanol (10 cc.) at room temperature and ether (10 cc.) was added. After the solution had remained in the refrigerator for 2 hours, the crystals (m.p. 98–101° C.) were removed by filtration, yield 1.31 g. (49.1%). One crystallization from ethanol-ether raised the melting point to 100–101° C. Anal. Calc. for $C_7H_{13}N_5O_5$: C, 34.00; H, 5.30; N, 28.33%. Found: C, 34.01; H, 5.46; N, 28.16%.

A picrate (m.p. 143.5–144.5° C.) of this compound was prepared in 63% yield in water in the usual manner. Two crystallizations from water raised the melting point to 144–144.5° C. Anal. Calc. for $C_{13}H_{15}N_5O_9$: C, 37.78; H, 3.66; N, 23.73%. Found: C, 38.17; H, 3.73; N, 24.03%.

1-Nitro- Δ^9 -1,5,9-triazabicyclo(4.4.0)decene nitrate (297.6 mg.) in absolute ethanol (20 cc.) was refluxed for 2½ hours. After the ethanol was removed *in vacuo* under nitrogen, crystals (m.p. 99–101° C.) were obtained, yield 272 mg. (91.6%). These crystals on admixture with the starting material did not depress the melting point.

Nitration of Δ^8 -Hexahydro-1,4,8-pyrimidazole

Δ^8 -Hexahydro-1,4,8-pyrimidazole (3.75 g., 0.03 mole) was nitrated in nitric acid-acetic anhydride medium and isolated under conditions similar to those described above in the preparation of 1-nitro- Δ^9 -1,5,9-triazabicyclo(4.4.0)decene nitrate.

The oily product crystallized on drying *in vacuo* over phosphorus pentoxide, yield 3.24 g. (46.3%). The melting point was raised from 143.5–145.5° C. to 145.5–146° C. by one crystallization from ethanol. Anal. Calc. for $C_6H_{11}N_5O_5$: C, 30.90; H, 4.76; N, 30.00%. Found: C, 31.15; H, 4.86; N, 29.94%. 1-Nitro- Δ^8 -hexahydro-1,4,8-pyrimidazole nitrate (m.p. 145–146° C.) was recovered unchanged after it had been refluxed in ethanol solution for 2½ hours.

Nitration of Δ^9 -1,4,9-Triazabicyclo(5.3.0)decene

Δ^9 -1,4,9-Triazabicyclo(5.3.0)decene (1.39 g., 0.01 mole) was nitrated in nitric acid-acetic anhydride medium under the conditions described above for the nitration of Δ^9 -1,5,9-triazabicyclo(4.4.0)decene. When the reaction mixture was poured into cold ether, crystals (m.p. 163–165° C.) separated immediately. The yield was quantitative. Three crystallizations from ethanol-ether solution raised the melting point to 166.5–167.5° C. Anal. Calc. for $C_7H_{13}N_5O_5$: C, 34.00; H, 5.30; N, 28.33%. Found: C, 33.99; H, 5.32; N, 27.76%.

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THE HEAT CAPACITIES OF THE CRYSTALLINE AND VACUUM DEHYDRATED FORM OF MAGNESIUM SULPHATE MONOHYDRATE¹

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ABSTRACT

Dehydration, under vacuum, of magnesium sulphate heptahydrate yields a product of monohydrate composition which does not give a diffraction pattern on X-ray examination and therefore has no evident crystalline structure. The heat capacity of this product has been determined over the temperature range from 90° K. to room temperature, and has been found to be substantially higher than that of the normal crystalline monohydrate. Consideration of these differences in heat capacity in conjunction with surface area data indicates that vacuum dehydration does not result in the formation of microcrystals the surfaces of which are available for gas adsorption. It is possible that aggregates of closely packed crystallites are formed in localized regions, these being interspersed with capillaries. Alternatively, it is possible that vacuum dehydration results in an intermediate state of ionic disorder.

INTRODUCTION

It has been pointed out in previous studies (7, 13) that when certain hydrated salts are dehydrated under vacuum, products are obtained which do not yield a pattern of diffraction lines on X-ray examination. These products usually have the stoichiometric composition of the monohydrates but have high energy contents with reference to their crystalline counterparts. Discussion of points of view regarding their nature has been given elsewhere (14, 3). Garner (4) has suggested that the phases prepared by vacuum dehydration may consist of extremely small crystallites below the limit in size (about 100 Å) required for the obtaining of an X-ray diffraction pattern, and so separated in space that they cannot readily grow to larger units. Alternatively, it is possible that, with the removal of water molecules, the lattice collapses into a disordered structure in which some or all of the ions are displaced from the positions they would occupy in the perfect lattice. Hence, the long range order characterized by the periodicity of a crystalline lattice structure would be lacking. On either of these points of view a difference in heat capacity between the normal crystalline monohydrates and those prepared by vacuum dehydration might be expected. The present work was undertaken in order to ascertain whether or not such differences in heat capacity are observable and if they are to attempt to assess their significance in relation to the nature of these products.

In this paper, data are reported for magnesium sulphate monohydrate in the temperature range between 90° K. and room temperature. The behavior of magnesium sulphate heptahydrate on dehydration at low ambient pressure of water vapor has been reported (2). Vacuum dehydration yields a product of monohydrate composition which does not diffract X-rays. This product is suitable for heat capacity determinations in that it is much more stable than those obtained by the dehydration of other salts, and may be subjected to such operations as transfer without change in weight or composition and without the occurrence of crystallization. Adsorption of gases at room temperature is negligible (13). After the product is heated for several days at about 160° C., the characteristic monohydrate (kieserite) diffraction lines are observed. This crystalliza-

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tion occurs without loss in weight or change in composition, making it possible to carry out heat capacity determinations on the same sample before and after crystallization.

EXPERIMENTAL METHOD

Preparation of Samples

Reagent grade magnesium sulphate heptahydrate was recrystallized, dried, and screened, the "through 60 on 80 mesh" portions being used. The vessel used for vacuum dehydration consisted of a set of concentric cylinders made from 100 mesh copper gauze, the alternate annular spaces being filled. The over-all cylinder was 5 cm. in diameter and 15 cm. long, four annular beds being provided, each about 3 mm. thick and separated from the next by a space also about 3 mm. wide. This vessel was contained in a closed glass tube with access to the usual type of vacuum line through a large ground-glass joint. Dehydrations were carried out for 5 days at $60 \pm 0.2^\circ \text{C}$.

Subsequent to heat capacity determinations on this material, crystallization was effected by quickly transferring the contents of the calorimeter to a glass-stoppered flask and heating for about 4 days at 160°C .

The Calorimeter Assembly

The thermometer mounting and the calorimeter vessel are shown in Fig. 1. A calibrated Leeds and Northrup 8164 platinum resistance thermometer and a heater made of glass-insulated manganin wire were embedded in a low melting alloy in a brass case $1/32$ in. thick. In order to ensure that as short a time as possible would elapse between the filling of the calorimeter and the assembly of the apparatus, this case was permanently mounted and provision made so that the calorimeter vessel, after being filled, could be slipped over the thermometer case. To this end, the case was lapped to a very accurate sliding fit into a brass thermometer well of the same thickness in the calorimeter vessel. In order to remove trapped air, a shallow groove was cut lengthwise along the side of the support.

In filling, the calorimeter vessel was inverted from the position shown in Fig. 1, and the sample quickly added and interspaced with a series of seven perforated copper disks which fitted closely around the outside of the thermometer well and came to within about $1/8$ in. of the outside wall of the vessel. The lid of the calorimeter vessel had a rim which fitted into a groove machined around the top of the calorimeter wall. A threaded ring was screwed over the lid to provide mechanical strength. After it had been filled, the calorimeter vessel was thoroughly evacuated and helium admitted for thermal conductivity; these operations were carried out by means of a Kovar metal-to-glass seal, soldered to a small perforation in the center of the lid. The mass of the calorimeter vessel was about 113 g.

The entire assembly showing the calorimeter suspension, adiabatic shield, and outer casing is shown diagrammatically in Fig. 2. A brass ring about 1 in. wide and $1/8$ in. thick was fitted around the top of the outside case. All leads coming from the shield were wrapped non-inductively around this ring before leaving the case by way of the exhaust tube on the top.

A large Dewar flask placed around the case contained the appropriate refrigerant. After a sufficient number of energy increments to raise the calorimeter to about 50°C . above the temperature of the bath, the coolant was removed, the empty Dewar flask replaced, and the case temperature allowed to slowly rise. Large thermal heads were thereby avoided.

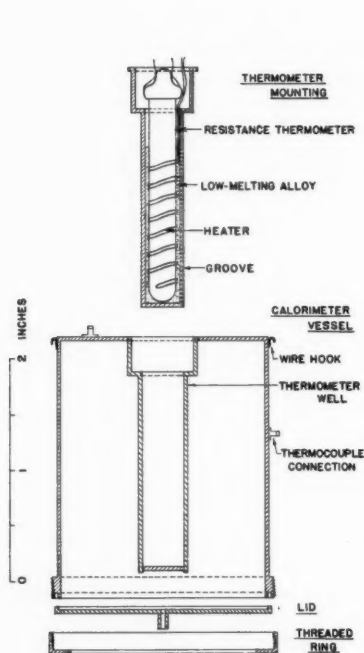


FIG. 1. Calorimeter vessel.

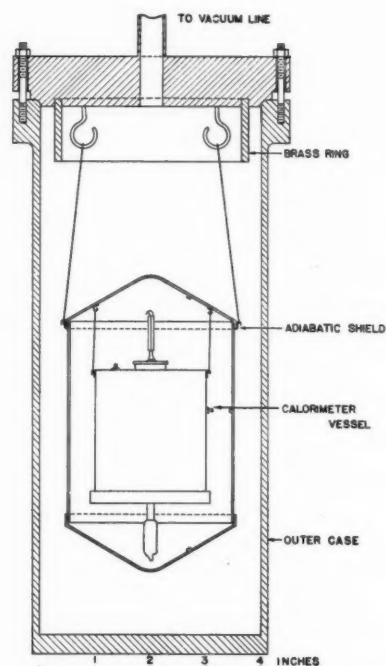


FIG. 2. Calorimeter assembly.

It was found that thermal equilibrium was reached in about 20 minutes. In some measurements the afterperiods were extended to about 60 minutes, no significant change in heat capacity being observed. Energy measurements were made on a White double potentiometer and temperature measurements on a G-2 Mueller bridge.

RESULTS

Heat Capacity of the Empty Calorimeter

Eight heat capacity determinations on the empty calorimeter over the whole or part of the range from 90° K. to 350° K. were carried out over a period of 6 months, as well as one set of determinations over the range from 0° C. to 60° C., using benzoic acid as a standard substance. The mean precision in these measurements was estimated to be about 0.15%. The heat capacity of the empty calorimeter was approximately equal to that of the contained material.

Heat Capacity of Magnesium Sulphate Monohydrate

A sample of 65.899 g. was prepared by vacuum dehydration, as described above. This sample was found by analysis to have the composition $\text{MgSO}_4 \cdot 0.88\text{H}_2\text{O} \pm 0.02$ moles of water. No diffraction lines were observed on X-ray examination. The experimental heat capacity values were corrected to correspond to the exact monohydrate composition from the values for the heat capacity of anhydrous magnesium sulphate reported by Moore and Kelley (11). A slight error may be introduced by this procedure in that the data of Moore and Kelley are for macrocrystalline material whereas the

small amount of anhydrous magnesium sulphate formed in dehydration is probably finely divided. At the conclusion of the heat capacity measurements X-ray powder photographs were again taken and no evidence of crystallization observed. The results are reported in the upper curve of Fig. 3.

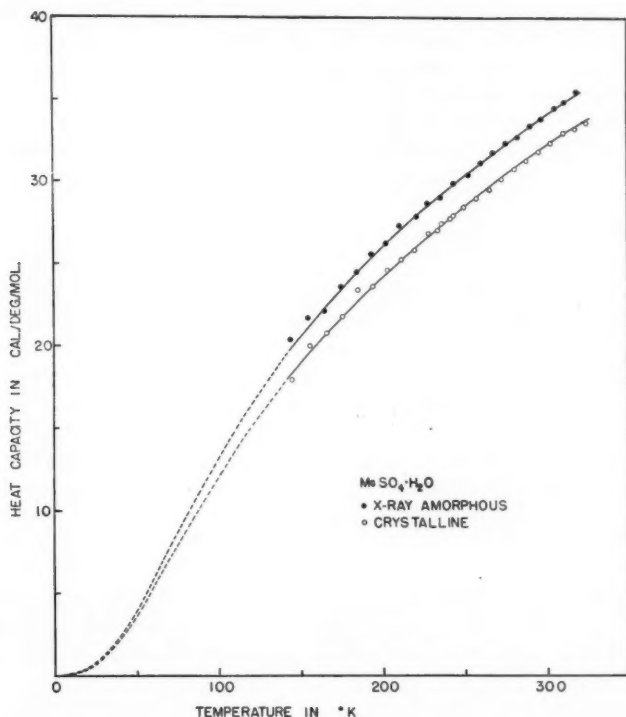


FIG. 3. Heat capacity of vacuum dehydrated (X-ray amorphous) and crystalline magnesium sulphate monohydrate.

The sample from the foregoing experiment was then crystallized, as has been described. No change in composition was detected by analysis. X-Ray examination showed a clear pattern of the characteristic kieserite lines. Heat capacity values, corrected as before to the exact monohydrate composition, are shown in the lower curve of Fig. 3.

As with the empty calorimeter, the mean precision in the actual measurement of the total heat capacity was estimated to be about 0.15%. Since the heat capacity of the empty calorimeter was approximately equal to that of the contained material, the precision in the experimental values for the latter is about 0.3%. However, there is an analytical uncertainty in the water content of 0.02 moles of water per formula weight of sample. As a result of this uncertainty the curves of Fig. 3 may be shifted up or down by about 0.5%, which corresponds to somewhat less than 0.2 heat capacity units. Since, however, the two samples were identical in composition, the difference between the heat capacities at any temperature is not likely to be affected by this analytical error. The values reported in Fig. 3 were checked by another complete series of measurements

on vacuum dehydrated and crystalline salts and the average mean deviation was found to be less than 0.5%.

It is clear from Fig. 3 that the heat capacity of magnesium sulphate monohydrate prepared by vacuum dehydration is substantially higher than that of its crystalline counterpart over the range of temperature in which measurements were made. Although the necessary extrapolations are very long, it will be found useful to obtain an estimate of the difference in entropy between the two forms, on the assumption that vacuum dehydration yields very small crystals which nevertheless approximate a perfect crystalline structure, and approach zero entropy at 0° K.

Moore and Kelley (11) have found that the heat capacity of anhydrous magnesium sulphate over the range 51° K. to 298° K. is fitted by the function sum:

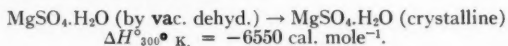
$$D(242/T) + 2E(378/T) + 2E(866/T) + E(1683/T).$$

By extrapolating their curve to 0° K. on the basis of this function sum and using this curve to extrapolate the data for magnesium sulphate monohydrate by the method of Kelley, Parks, and Huffman (10), a provisional value of the entropy of crystalline magnesium sulphate monohydrate is found to be 30.2 e.u. by graphic integration. The heat capacity curve for the monohydrate obtained by vacuum dehydration may be extrapolated by the same procedure, which leads to an entropy value of 33.0 e.u. Hence, for the transition from the normal crystalline state to that assumed to be microcrystalline, $\Delta S_{298^\circ \text{K.}} = 2.8$ e.u. On account of the long extrapolations (indicated by the dotted curves of Fig. 3) no very accurate estimate can be made of the uncertainty in this value, which is of interest only in giving some idea of the entropy change involved if the product of vacuum dehydration is microcrystalline.

DISCUSSION

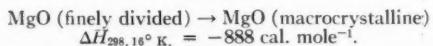
Before attempting to assess the significance of these results in throwing light upon the nature of the product of vacuum dehydration, it will be desirable to compare the differences in heat capacity with those observed for other substances for which measurements have been made, and to consider these comparisons in the light of known data regarding heats of transition and surface areas.

From comparison of the heat of solution of magnesium sulphate monohydrate prepared from the vacuum dehydration of the heptahydrate with that of the crystalline monohydrate, Jamieson and Frost (7) obtained:



Quinn, Missen, and Frost (13) reported a surface area of approximately 8 m.² g.⁻¹ for the product of vacuum dehydration.

Calorimetric measurements, similar to the foregoing, were carried out by Giauque and others on the heat of solution in hydrochloric acid of normal crystalline magnesium oxide, and of finely divided magnesium oxide prepared by the vacuum dehydration of crystalline magnesium hydroxide. From these measurements, Giauque (5) has reported:



The nitrogen adsorption surface area of finely divided magnesium oxide prepared in this manner has been reported by Jura and Garland (8) as 86 m.² g.⁻¹. The X-ray dif-

fraction pattern agreed with the known lattice parameters of the macrocrystalline material. The heat capacity of this material was found by Giauque and Archibald (6) to be higher than that of the crystalline material, the differences being about 1% at ordinary temperatures and about 6% at 90° K., which implies a nearly constant difference in heat capacity over this range. Giauque estimated that the finely divided material had a larger entropy than the macrocrystalline material by about 0.2 cal. deg.⁻¹ mole⁻¹.

Dugdale, Morrison, and Patterson (1) determined the heat capacity of titanium dioxide samples of specific surface 8.5, 9.5, 55, and 100 m.² g.⁻¹ and found a pronounced difference in the range of temperature between 50° K. and 270° K. Patterson (12) has estimated that about one-fifth of this observed difference can be accounted for by differences in particle size. A comparison of available data for these substances is given in Table I.

TABLE I

Formula	Powder photograph	Heat transition, cal. g. ⁻¹	Specific surface, m. ² g. ⁻¹	Heat transition, cal. m. ⁻²	Per cent difference in heat cap.	Per cent difference per m. ² × 10 ²
MgO	Diffraction lines	22.2	86	0.26	1 (298° K.) 6 (90° K.)	1 7
TiO ₂	Diffraction lines	(No data)	100	(No data)	3 (298° K.) 2 (90° K.)	3 2
MgSO ₄ ·H ₂ O	Diffuse halo	47	8	5.9	6 (298° K.) 9 (90° K.)	75 110

The high values of the heat of transition per unit surface and of the per cent differences in heat capacity per unit surface for magnesium sulphate monohydrate in comparison with those of the other substances are, of course, due to the very much lower surface area. In this respect, the following consideration is also of interest.

Assuming that the observed differences in heat capacity and heat of solution of coarse and fine particles of magnesium oxide are extensive properties of the surface and that the entropy of both materials approaches zero at 0° K., Jura and Garland (8) calculated the surface free energy of magnesium oxide obtaining values ranging from 1040 to 1000 ergs cm.⁻² over the temperature interval from 0° K. to 298° K. If the values of the heat of transition, surface area, and entropy difference given in the foregoing are used to calculate the surface free energy of magnesium sulphate monohydrate, values are obtained which are over 20 times greater than those obtained for magnesium oxide. In this calculation, the heat of transition is accurately known, and uncertainty in the value of the entropy change does not change the result in any significant way. It follows that the adsorption surface area does not measure the area of the microcrystals if such are formed.

Consideration may now be given to the nature of the product of vacuum dehydration in the light of these data. If vacuum dehydration results in the formation of microcrystals, these must be below the limit in size required for X-ray diffraction (about 100 Å). If these are so separated in space that they cannot readily grow to larger units, the formation of such a microcrystalline structure would result in a large increase in boundary, and the lower vibrational frequencies at the boundary would lead to an increase in heat capacity relative to the macrocrystalline phase. However, such a structure would have a very large specific surface. The diameter of the particles of magnesium

oxide used in the heat capacity determinations of Giauque and Archibald was about 200 \AA (9), or therefore about twice the size limit below which diffraction would not be observed. Quinn, Missen, and Frost (13) found that the product obtained by vacuum dehydration of magnesium sulphate heptahydrate was interspersed with capillaries ranging in diameter from about 11 \AA to 26 \AA and that the total capillary volume is small. The surface area of approximately $8 \text{ m}^2 \text{ g}^{-1}$ is undoubtedly that due to this capillary structure, and does not measure the area of the individual particles as in the case for finely divided magnesium oxide. Since these are probably much smaller than the capillary diameters, it is possible that they may consist of only a few unit cells. It would appear, then, that as dehydration proceeds from nucleated points on the crystal surface, contraction occurs resulting in capillary formation, the regions between the capillaries being closely packed with a disordered assembly of minute crystallites which are not accessible to the gas used in the determination of surface area. The thermodynamic properties of such an assembly would not be extensive in the surface, and it is difficult to estimate whether or not such an assembly would give heat capacity differences of the magnitude of those observed relative to the macrocrystalline state.

Alternatively, it is possible that vacuum dehydration does not result in the formation of monohydrate crystallites as entities, but that on the removal of water molecules the lattice structure collapses into an intermediate state which crystallizes into the kieserite structure under the proper conditions. This intermediate state might be visualized as a disordered arrangement in which some or all of the ions are displaced from the positions they would occupy in the perfect lattice. The lessening of the proximity of oppositely charged ions and the over-all repulsive effect of ions of like charge will give rise to a range of weaker average bond strengths than would be found in the corresponding crystalline state. Consequently, the average frequency of the thermal vibrations will be lower, resulting in a higher heat capacity.

Such a disordered structure should be thermodynamically unstable with respect to the corresponding crystalline form, and under conditions which give mobility to the ions should crystallize with an evolution of energy equal to the difference in heats of solution between the amorphous and crystalline forms. Such a spontaneous energy release following the vacuum dehydration of several hydrated salts has been observed (3). On the basis of this interpretation the surface areas as determined by gas adsorption are valid, but the structure of the phase interspersed by capillaries is ionically disordered, resulting in internal strain which would be manifested by an observable difference in thermodynamic properties. If this interpretation is correct an indeterminable zero-point entropy would exist, and the evaluation of the absolute entropy of the vacuum dehydrated material from the extrapolated heat capacity curve would not be justified.

Experiments of an exploratory character indicate that for other salts, such as copper sulphate pentahydrate, vacuum dehydration yields products lacking in crystallographic character which have higher heat capacities than their crystalline counterparts, the differences being comparable to those given in the foregoing and subject to the same interpretation.

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N-ACYL SUBSTITUTED PHENYLHYDROXYLAMINES: THE EFFECT OF RADICAL CHANGE ON ANALYTICAL BEHAVIOR¹

C. A. ARMOUR AND D. E. RYAN

ABSTRACT

The synthesis of a number of N-acyl substituted phenylhydroxylamines is outlined and the effect of the change in the nature of the acyl group on their usefulness as analytical reagents is described. Stability constant measurements in alcohol show an increase in stability with an increase in basicity of reagent regardless of the nature of the attached group; their ability to precipitate complexes from aqueous solution, however, is markedly dependent on the nature of the attached radical. A spectrophotometric study shows the existence of both a 1:1 and a 1:3 iron complex. A more sensitive colorimetric reagent results with an unsaturated five-membered ring as the attached grouping.

INTRODUCTION

N-Benzoylphenylhydroxylamine has been used as an organoanalytical reagent for the determination of iron, aluminum, copper, and titanium (4); for tin (3); for vanadium (5); and for tantalum (2). It has been recommended as superior to cupferron, when applicable, because it is much more stable to heat and light and forms complexes that can, in many instances, be dried at 110° C.

The reactions of seven other acyl substituted phenylhydroxylamines were discussed in another paper by Lutwick and Ryan (1). Their results showed that variations in the nature of the ring attached to the carbonyl group, alpha to the oxime, gave some variation in the conditions for reaction with metal ions. In order to study more fully the effect of ring closure and changes in the nature of the ring, a further series of mono N-acyl derivatives of phenylhydroxylamine were prepared and their reactivity investigated.

COMPOUNDS INVESTIGATED

The following derivatives were prepared: hexanoyl ($C_6H_{11}C=O$), heptanoyl ($C_6H_{13}-C=O$), cyclohexanoyl ($C_6H_{11}C=O$), benzoyl ($C_6H_5C=O$), nicotinyl ($C_6H_4NC=O$), thenoyl ($C_6H_5SC=O$), and furoyl ($C_4H_5OC=O$), and the acetyl derivative



of hydroxylamine ($CH_3-C-N-H$). The phenylhydroxylamine compounds were synthesized by the slow addition of their acid chlorides (prepared when not available by refluxing the corresponding acid with thionyl chloride for an hour and separating by distillation) to an ether solution of phenylhydroxylamine; pyridine was added to maintain the pH at 7. The main bulk of the derivative dissolved in the ether solution; the excess pyridine that had not settled out as hydrochloride was removed by extraction with dilute hydrochloric acid.

The aromatic derivatives—benzoyl, furoyl, and thenoyl—were obtained by the addition of heptane to the ether solution; it was necessary to cool the ether solution of the aliphatic derivatives—hexanoyl, heptanoyl, and cyclohexanoyl—in a dry ice bath to obtain the crude product. Extraction of the crude product with concentrated ammonium hydroxide, in which any disubstituted product is insoluble, yielded the monoderivative on acidification with 3 N hydrochloric acid. The compounds were recrystallized from ether by the addition of heptane and cooling in a dry ice bath.

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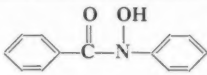
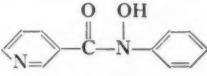
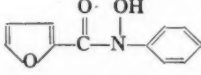
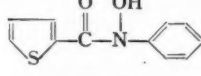
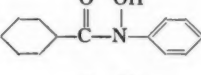
Contribution from the Department of Chemistry, Dalhousie University, Halifax, N.S., with financial assistance from the National Research Council. Abstracted from the M.Sc. thesis of C. A. Armour.

The product of the reaction between nicotiny chloride and phenylhydroxylamine is the hydrochloride of nicotinyphenylhydroxylamine which settles out of the ether solution when no pyridine is present. The pure nicotiny derivative is obtained by dissolving the solid in concentrated ammonium hydroxide, neutralizing with 3 *N* hydrochloric acid, extracting repeatedly with ether, and cooling in a dry ice bath.

Properties of Compounds

Table I shows the melting points and structural formulae of these compounds, which are all white solids. Their chemical properties are similar to those previously reported (1); however, there is a marked difference in the ability of the products of reaction to separate from aqueous solution.

TABLE I

Compound	Structural formula	M.p., ° C.
N-Benzoylphenylhydroxylamine		121
N-Nicotinyphenylhydroxylamine		134
N-Furoylphenylhydroxylamine		134
N-Thenoylphenylhydroxylamine		97
N-Cyclohexanoylphenylhydroxylamine		124
N-Hexanoylphenylhydroxylamine	$\text{CH}_3(\text{CH}_2)_4\text{CH}-\text{C}(=\text{O})\text{N}(\text{OH})\text{C}_6\text{H}_5$	67
N-Heptanoylphenylhydroxylamine	$\text{CH}_3(\text{CH}_2)_5\text{CH}-\text{C}(=\text{O})\text{N}(\text{OH})\text{C}_6\text{H}_5$	60
N-Acetylhydroxylamine	$\text{CH}_3\text{C}(=\text{O})\text{N}(\text{OH})\text{H}$	30

Benzoyl, thenoyl, and furoyl phenylhydroxylamines give good precipitates in solutions greater than 1% concentrated hydrochloric acid with Sn^{4+} , Sn^{2+} , Ti^{4+} , Zr^{4+} , and V^{5+} (as VO_4^{3-}). The aliphatic compounds—hexanoyl, heptanoyl, and cyclohexanoyl—react to give cloudy, non-filterable products. Nicotinyphenylhydroxylamine reacts to give soluble complexes due to the formation of hydrochloride salts.

All reagents give a deep purple solution with iron at pH 2; a further increase in acidity destroys the complex. On addition of sodium acetate, the aromatic derivatives—benzoyl, thenoyl, furoyl, and nicotiny—yield thick reddish brown precipitates of the 1:3 iron chelate (soluble in organic solvents); the aliphatic derivatives produce a reddish brown

suspension which, on standing, settles out as an oil for the hexanoyl and heptanoyl compounds and as a fine precipitate for the cyclohexanoyl derivative. Acetylhydroxylamine yields an orange water-soluble product.

Copper reacts with all the reagents to give a green solution or precipitate depending on pH. At pH 4, immediate precipitation of a thick light green solid was obtained with all the aromatic derivatives. The bluish green solids obtained with the aliphatic derivatives were precipitated slowly and were contaminated with large amounts of reagent.

Reagent Acidity and Completeness of Precipitation

Lutwick and Ryan (1) found that, provided the nature of the ring attached to the carbonyl group of the oxime did not change, there is an increase in pH required for complete precipitation of copper with increase in reagent acidity. The results given in Table II show that this is no longer true when the nature of the ring is changed.

TABLE II

Compounds	pH of 1% solution of reagent in ethanol*	Lowest pH for complete precipitation of copper†
Benzoylphenylhydroxylamine	7.55	3.0
Hexanoylphenylhydroxylamine	7.30	4.5
Cyclohexanoylphenylhydroxylamine	7.25	4.5
Heptanoylphenylhydroxylamine	7.30	4.5
Furoylphenylhydroxylamine	6.85	3.0
Thenoylphenylhydroxylamine	6.85	3.0

*The pH of the 1% reagent in absolute ethanol was determined after passing nitrogen through the solution for 20 minutes before and also during the pH measurements.

†In the determination of pH for complete precipitation cuproin was used to test for copper in the filtrates.

This effect is even more pronounced in the iron precipitation. While precipitation is obtained at a pH of 3.5–4 for the benzoyl, thenoyl, and furoyl compounds, the aliphatic derivatives yield only an unfilterable oil or fine precipitate under the same conditions. In order to study more closely these derivatives, a detailed spectrophotometric investigation of the iron reaction was carried out.

THE IRON REACTION

As previously stated, iron reacts in aqueous solution with all the compounds to give a purple solution or reddish brown product, depending on pH. Absorption measurements were made with a Beckman Model DU Spectrophotometer using 1-cm. cells; all experiments were done in absolute ethanol since ferric chloride, reagent, and complexes are all soluble in this solvent.

The general absorption characteristics of the iron benzoylphenylhydroxylamine system were obtained in a series of experiments in which the pH was varied from 1 to 7 at constant iron concentration and a constant reagent/iron mole ratio of 6. The color of the solution changes from purple (at pH 1) to orange, there being a gradual shift in absorption spectra to the ultraviolet with increasing pH up to 4.8. Beyond 4.8 there is no shift in either absorption band or intensity and complete formation of the 1:3 iron chelate is indicated; the absorption spectrum obtained in this way was identical with that of an equivalent amount of the solid 1:3 iron benzoylphenylhydroxylamine dissolved in alcohol or carbon tetrachloride. Graphs B and C of Fig. 1 show the absorption spectra at pH 1.8 and 4.8 respectively.

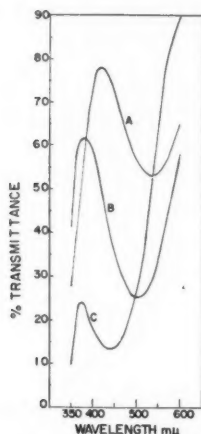


FIG. 1. Absorption characteristics of iron benzoylphenylhydroxylamine system: A, pH 1.75, mole ratio reagent/iron 0.9:1; B, pH 1.8, mole ratio reagent/iron 6:1; C, pH 7, mole ratio reagent/iron 6:1.

In a second series of experiments the absorption spectra were run on standard iron solutions to which had been added varying amounts of reagent, so that the molar ratio of reagent/iron varied from 0.3 to 6. From 0.3 to 0.9 the position of the absorption band remains constant (Graph A, Fig. 1) showing increased intensity with increased concentration of reagent. From 1 to 3 there is a gradual shift to the ultraviolet; from 3 to 6 the band again becomes stationary (Graph B, Fig. 1) showing a slight increase in intensity with increased concentration.

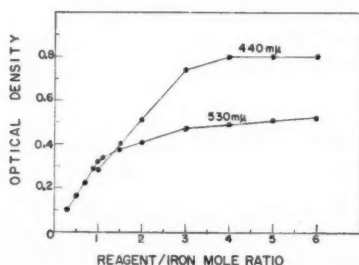


FIG. 2. Optical density at 530 and 440 $m\mu$ of the iron benzoylphenylhydroxylamine system as a function of the ratio reagent/iron; total iron concentration $1.79 \times 10^{-4} M$.

It is evident that both a stable 1:1 and a stable 1:3 iron complex exist in alcohol solution. Pure 1:1 complex is obtained at pH 1.7 when the molar concentration of reagent is less than that of iron; pure 1:3 complex is obtained between pH 4.8 and 7.

From Fig. 2 the increase in optical density at 530 $m\mu$ as reagent/iron mole ratio increases from 0.3 to 1, and a decrease in optical density as the mole ratio rises above 1, clearly shows the formation of a 1:1 complex. Similarly Fig. 2 shows the existence of a 1:3 complex at 440 $m\mu$.

Stability Constants

To determine the stability constant for the 1:1 iron benzoylphenylhydroxylamine

complex two solutions were prepared having the same optical density but different quantities of reagent and iron. From the equation

$$K = x/[(\text{Fe}_1 - x)(\text{Reag}_1 - x)] = x/[(\text{Fe}_2 - x)(\text{Reag}_2 - x)],$$

both chelate concentration x and stability constant K can be calculated. The stability constant was found to be 1.9×10^5 .

The absorption spectra of the 1:3 iron complexes in alcohol for all reagents prepared are shown in Fig. 3.

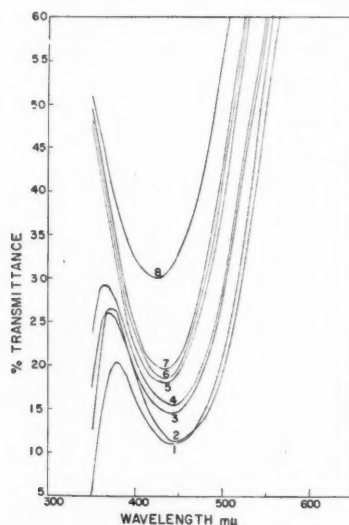


FIG. 3. Absorption characteristics of 1:3 iron chelates: 1, thenoyl; 2, furoyl; 3, nicotinyl; 4, benzoyl; 5, hexanoyl; 6, cyclohexanoyl; 7, heptanoyl-phenylhydroxylamine; 8, acetylhydroxylamine.

Since the 1:3 iron complexes in alcohol obey Beer's law, it is possible to calculate their stability constants provided 100% formation of the chelate is obtained with a large excess of reagent present. As complete formation of the 1:3 complex occurs at a 6:1 but not a 3:1 mole ratio of reagent/iron, measurements of optical densities at these concentrations permit the calculation of stability constants. The values shown in Table III are only approximate since any reagent weighing errors are much magnified in the stability constant expression

$$K = (\text{chelate})/[(\text{iron})(\text{reagent})^3].$$

A sample calculation, in which the molar concentration of iron was 1.79×10^{-4} , is shown below:

Mole ratio reagent/iron	Optical density	Chelate concentration
6:1	0.805	1.79×10^{-4}
3:1	0.740	1.64×10^{-4}

$$K = (\text{chelate})/[(\text{iron})(\text{reagent})^3] = (1.64 \times 10^{-4})/[(0.15 \times 10^{-4})(0.45 \times 10^{-4})^3] = 1.2 \times 10^{14},$$

$\log K = 14.1$.

Table III also gives the values of the molecular extinction coefficient in the region of maximum absorption.

TABLE III
STABILITY CONSTANTS AND MOLECULAR EXTINCTION
COEFFICIENTS OF 1:3 IRON CHELATES

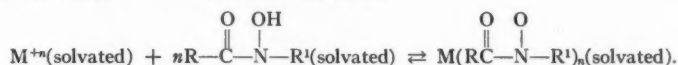
N-Acyl derivative	Log K	ϵ
Benzoyl	14.1	4495
Heptanoyl	14.0	3920
Hexanoyl	13.6	3965
Cyclohexanoyl	13.6	4065
Nicotinyl	13.1	4580
Furoyl	12.8	5180
Thenoyl	12.5	5295

These results show that the stability constants, measured in alcohol, decrease as the acidity of the reagents increases (see Table II); the stability of the complexes in alcohol seems solely dependent on the acidic property of the reagent and not on the nature of the ring attached to the carbonyl grouping. The nature of the ring does, however, affect the ability to precipitate the complex from aqueous solution.

The intensity, as exemplified by molecular extinction coefficients, is naturally dependent on the nature of the attached groupings. The molecular extinction coefficients increase with an increase in the extent of the π system; as is expected, acetylhydroxylamine, which has no π electrons other than those of the metal chelate ring itself, has a much lower molecular extinction coefficient (2700).

DISCUSSION

The study of these compounds shows the danger of attempting to correlate stability constants determined in non-aqueous solvents with their usefulness as precipitants. In non-aqueous solutions the reaction involved is:



In aqueous solution there is additional energy required in order to squeeze out the solvent molecules and permit crystal forces to act to bring about precipitation. In the N-acyl substituted phenylhydroxylamines there is a marked difference in the lattice energies of the chelate; the crystal energy - solvation energy difference of the thenoyl and furoyl derivatives is greater than the benzoyl compound, as shown by the fact that, while their stability constants in alcohol are lower, the pH for complete precipitation is similar to that of benzoylphenylhydroxylamine. Since the aliphatic compounds—hexanoyl, heptanoyl, and cyclohexanoyl phenylhydroxylamines—give oils or poorly defined crystals from aqueous solution, their lattice energy must be insufficient to bring about suitable crystallization.

In the aromatic derivatives, since each reagent molecule is planar and iron forms octahedral complexes, the three chelating rings will be at right angles (Fig. 4) and arrangement of the molecules for good crystal bonds is possible. Replacing one aromatic ring by an aliphatic group destroys the planar nature of the ligand ring and its π system preventing good crystal formation. The difference in the ability of the aliphatic and aromatic derivatives to precipitate complexes from aqueous solution is shown, not

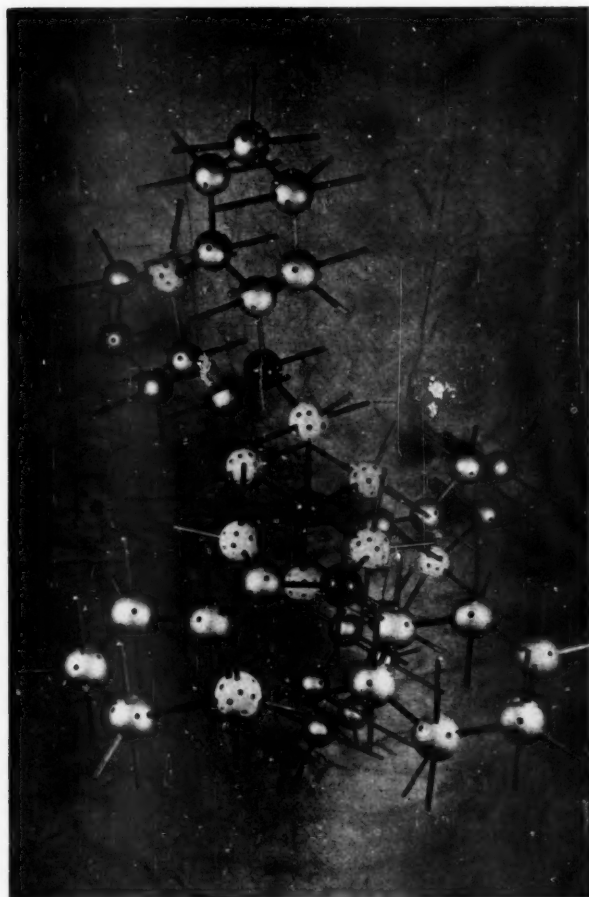


FIG. 4. Model of 1:3 iron furoylphenylhydroxylamine chelate showing planar structure of the ligand molecules and their position in the complex; lines on each atom perpendicular to the planes of the rings represent π electrons.

only from the stability data with iron, but also from their reactions with the other metal ions studied.

The new N-acyl substituted phenylhydroxylamines investigated show no advantage over the benzoyl derivative in reactions in aqueous solution. However the increased sensitivity of the color reaction obtained in alcohol with the five-membered ring substituted compounds suggests that for colorimetric determinations the use of furoyl or thenoyl derivatives is preferred.

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SEPARATION OF ENDOMYCINS A AND B, AND THEIR IDENTIFICATION AS MEMBERS OF THE POLYENE GROUPS OF ANTIFUNGAL ANTIBIOTICS¹

L. C. VINING AND W. A. TABER

ABSTRACT

An unidentified *Streptomyces* species isolated from platings of "honey dew" of the fungus *Claviceps purpurea* produced two antifungal antibiotics which were shown by paper chromatography to be identical with the two active components of endomycin, and also with helixins A and B. An examination of the ultraviolet absorption spectra of the three complexes showed maxima at wavelengths associated with two unsaturated systems containing four and six conjugated double bonds respectively. The two unsaturated components were separated by countercurrent distribution and shown to correspond to the two active fractions. The tetraene has been named endomycin A, and the hexaene endomycin B. Flavacid, a polyene complex also containing tetraene and hexaene components, is not identical with endomycin.

The isolation of a new antifungal agent which was given the name endomycin was reported by Gottlieb and his co-workers in 1951 (3). The organism producing this substance was considered at that time to be a new species and was given the name *Streptomyces endus* although a recent taxonomic study (8) has suggested its inclusion within the established species *Streptomyces hygroscopicus*. In spite of extensive attempts at purification, the product was not obtained crystalline and no effort was made to characterize the active factors chemically. In a subsequent publication describing methods for the paper chromatographic separation of antifungal antibiotics, Ammann and Gottlieb (1) have reported a single R_f value of 0.69 for endomycin in water-saturated *n*-butanol. Other substances characterized by their R_f values in this solvent were the "polyene" antibiotics, nystatin (0.25), rimocidin (0.39), candicidin (0.44), and ascocin and trichomycin (0.33–0.35).

Almost simultaneously, an antifungal agent with very similar biological and chemical behavior was reported by Leben and co-workers (4). This substance, isolated from an unnamed *Streptomyces* by a procedure analogous to that used for endomycin, was given the name helixin, although it was recognized that the crude product obtained at that time might prove to contain more than one antibiotic. A subsequent paper chromatographic study (7) established that there were indeed four active components present. These were designated helixins A, B, C, and D, and appeared on paper chromatograms run in a water-saturated mixture of equal parts of *n*-butanol and ethyl acetate at R_f 's 0.07, 0.42, 0.85, and 0.68 respectively. Helixin D could not always be detected in the crude preparation and appeared to be only a minor component. Helixin C could be separated from the mixture by extraction with ethylene dichloride. Comparison of a purified helixin sample containing components A and B with endomycin showed no important differences in antimicrobial activity against a range of organisms, and endomycin was found to give two active fractions upon paper chromatography in the above solvent mixture at the same R_f values as helixins A and B. A trace of an active component corresponding to helixin D was occasionally observed, and it was noted that the proportion of the component corresponding to A in the endomycin mixture was considerably smaller than for helixin.

In this laboratory recently there was isolated from platings of "honey dew" of *Claviceps*

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purpurea obtained from naturally infected rye a species of *Streptomyces* (PRL 1678) which produced in liquid culture on a soybean meal - cerelose medium a highly active antifungal substance. The activity was found to be about equally divided between broth and mycelium and was concentrated by a procedure identical with that used for the isolation of candidin (11). The crude material so obtained was a yellowish brown powder, partially soluble in methanol and ethanol, but readily soluble in alcohols containing 10-20% of water. It was also very soluble in dimethylformamide, pyridine, or glacial acetic acid, but insoluble in acetone, chloroform, benzene, and other non-polar solvents. Although insoluble in water and sodium bicarbonate solution, it was dissolved in 0.02 *N* sodium hydroxide or hydrochloric acid solutions. These properties and the method of isolation suggested a similarity to the endomycin-helixin complex on the one hand, and on the other to the well-known group of polyene antifungal antibiotics commonly found in *Streptomyces* species (6). Examination of the ultraviolet absorption spectrum (Fig. 1) confirmed the latter relationship and indicated that the product was a mixture containing tetraene and hexaene members of this series. An examination of the ultraviolet absorption spectra of samples of endomycin and helixin (Fig. 1) proved that these two substances also contained peaks at substantially the same positions, although it was apparent that a higher proportion of impurities with strong absorption in the lower wavelength region was present in both samples.

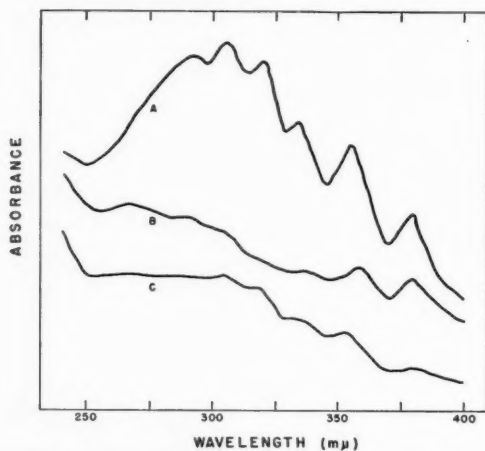


FIG. 1. Absorption spectra of the crude antibiotic preparations in ethanol. A, antibiotic from *Streptomyces* PRL 1678; B, endomycin; C, helixin.

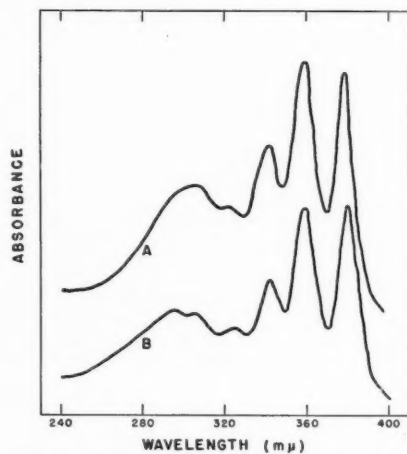


FIG. 2. Absorption spectra of medicidin and flavacid (redrawn from references cited in the text). A, medicidin in methanol; B, flavacid in ethanol.

Paper chromatography of the three samples in several solvent systems confirmed the report of Smeby *et al.* (7) that helixin and endomycin each contain two major components which are the same for both antibiotics, and also showed that these same two components are responsible for the activity of the product isolated in this laboratory. A summary of the R_f values obtained is given in Table I.

Of the known members of the "polyene" group of antibiotics, flavacid (6) and medicidin (9) contain the conjugated hexaene system. The published ultraviolet absorption spectrum of flavacid (Fig. 2) clearly shows that, in addition to the hexaene, a tetraene

TABLE I
 R_f VALUES OF VARIOUS TETRAENE AND HEXAENE ANTIBIOTICS

Antibiotic	Solvent system*				
	A	B	C	D	E
Endomycin	0.04, 0.37	0.03, 0.25	0.10, 0.38	0.30, 0.70	0.03, 0.29
Helixin	0.04, 0.37	0.02, 0.25	0.09, 0.38	0.31, 0.70	0.03, 0.30
Crude preparation from <i>Streptomyces</i> PRL 1678	0.05, 0.38	0.03, 0.25	0.09, 0.37	0.32, 0.72	0.03, 0.30
Flavacid	0.05	0.03	0.20	0.56	0.02
Tetraene component of <i>Streptomyces</i> PRL 1678	0.06	0.02	0.09	0.32	0.03
Hexaene component of <i>Streptomyces</i> PRL 1678	0.38	0.25	0.38	0.69	0.30

*The composition of the solvent systems was as follows: A, water-saturated *n*-butanol; B, water-saturated *n*-butanol on paper buffered with 0.1 *N* sodium carbonate; C, water-saturated *n*-butanol on paper buffered with 0.1 *N* sodium phosphate, pH 12.0; D, *t*-butanol-water (4:1); E, *n*-butanol-ethyl acetate (1:1) saturated with water.

component with peaks at 293, 306, and 324 $m\mu$ is present. A sample of flavacid compared directly on paper chromatograms with endomycin and helixin proved, however, not to be identical with these substances. Only one active zone was obtained, differing in R_f value from either of the endomycin and helixin components (Table I). The absence of a second active zone is accounted for by the fact that the tetraene components of these mixtures have considerably lower activity per unit weight against *Candida albicans* than the hexaenes, and since the latter forms the major part of the flavacid complex it is not possible to apply a large enough sample to the chromatogram to produce an active tetraene zone without causing severe streaking.

A sample of mediocidin was not available for comparison. However, it has already been reported by Utahara *et al.* (9) that a tetraene component is produced along with the hexaene by the cultures from which this antibiotic has been isolated. The presence of the two conjugated polyene systems in the crude mediocidin is seen in the published ultraviolet absorption spectrum (Fig. 2).

The separation into its components of a helixin preparation containing both A and B fractions by a single partition between ethyl acetate-*n*-butanol (1:1) and 0.06 *N* aqueous ammonia has been described by Smeby *et al.* (7). By this means helixin B could be recovered from the organic, and helixin A from the aqueous phase. We have been unable to obtain a complete separation of the components of the preparation obtained from *Streptomyces* PRL 1678 by this procedure, and paper chromatographic examination of a sample of helixin B prepared in this way showed that a small amount of the A component was still present. However, by countercurrent fractionation using the comparable solvent mixture ethyl acetate-*n*-propanol-0.1 *N* aqueous ammonium acetate (3:1:3) the two active components have been satisfactorily separated. The result of a 60-transfer fractionation is shown in Fig. 3. Solutions from tubes 6-20 and 30-46 were pooled separately and evaporated to dryness. The ultraviolet absorption spectra of these two fractions are given in Fig. 4 and indicate a clear separation of the conjugated tetraene and hexaene systems. When they were compared on paper chromatograms with the original material, each gave a single active zone (Table I). The tetraene was found to correspond with the slower moving zone using the solvent system of Leben *et al.*, and must therefore be identical with helixin A. Helixin B is the hexaene component.

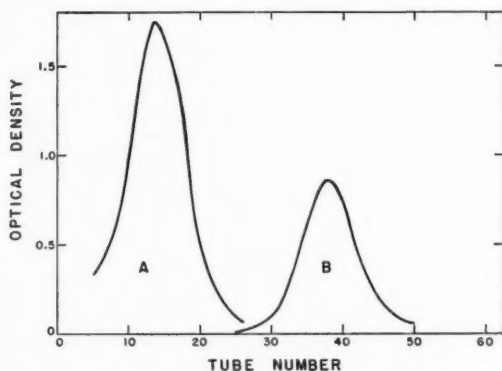


FIG. 3. Countercurrent distribution of antibiotic from *Streptomyces* PRL 1678. A, tetraene component, optical density measured at 320 $m\mu$; B, hexaene component, optical density measured at 380 $m\mu$.

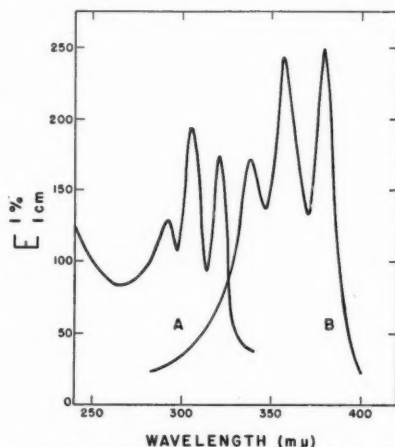


FIG. 4. Absorption spectra of fractions from countercurrent distribution. A, tubes 6-20 (endomycin A); B, tubes 30-46 (endomycin B).

These results together with the work of Leben and co-workers indicate that helixin and endomycin represent alternative names for an antibiotic complex, the two major components of which constitute additional members of the group of antifungal polyenes isolated from *Streptomyces* species. Since the name endomycin was first applied to this substance, and has been recognized in a review by Benedict (2), it is suggested that the tetraene and hexaene fractions be referred to as endomycins A and B respectively and that use of the term helixin be discontinued. Helixin C, since it was readily soluble in ethylene dichloride, undoubtedly represents a substance of quite different nature from the polyene components and is probably identical with the ether-soluble fraction produced by *Streptomyces endus* and referred to as antibiotic 9-20F-1 (3). Similar ether-soluble antifungal fractions have been reported in other polyene producing *Streptomyces* cultures (5) and may be closely related to each other. Although no evidence for the existence of this component in the mixtures was obtained during the present work, a very minor component running slightly ahead of B in most solvent systems was frequently observed. This is probably the D component found in helixin by Leben and co-workers, but has not been investigated.

The differences noted between the flavacid and endomycin complexes prove once again that structural variations among the polyene group of antibiotics are common, and are not confined to differences in the number of conjugated unsaturated bonds. The existence of at least four different tetraenes, three pentaenes, and four heptaenes has already been proved, and it has been shown that mixtures containing members with either the same (e.g. trichomycins A and B) or different (e.g. amphotericins A and B) numbers of conjugated double bonds may be produced by a single *Streptomyces* species.

From the intensity of the absorption maxima of the purest preparation of the endomycin complex available it could be calculated that not more than 9% of A and 3% of B were present in the mixture, and previous experience with "polyene" preparations (10) has shown us that further purification of material of this quality is not possible

without resorting to exacting methods of fractionation. No satisfactory chromatographic procedures for purification of these polyene antibiotics on a preparatory scale have yet been found. Countercurrent fractionation appears therefore to be the only method available for obtaining purified samples of endomycins A and B, and in the single distribution described above samples of approximately 20 and 17% purity, respectively, were recovered. By repeated fractionation, or the use of a larger number of transfers, pure samples might be obtained. However, in view of the limited solubility of crude endomycin in the solvent system used, the method was not considered practicable and a search for cultures producing the antibiotic complex free from most of the contaminating material appears to be a more fruitful approach.

EXPERIMENTAL

Production of Antibiotic from Streptomyces PRL 1678

A 5-gallon stirred tank containing a nutrient medium consisting of soybean meal (300 g.), cerelose (225 g.), and calcium carbonate (10 g.) in distilled water (15 liters) was inoculated with 1% of a 40 hour culture of *Streptomyces* PRL 1678 grown in shaken flasks on the same medium. After 4 days' growth at 28° C. at an aeration rate of 0.5 liter per liter per minute, the filtered broth contained 9000 dilution units per ml. when assayed against *Candida albicans* A.T.C.C. 10231 by the agar dilution method; the unit of activity adopted was the minimum amount of antibiotic which would completely inhibit the test organism.

The whole culture was treated with Hyflo supercel (2 kg.), acidified to pH 4.5 with 2 *N* hydrochloric acid, and filtered. The inactive filtrate was discarded and the residue extracted three times with 10 liters of 80% ethanol. After concentration *in vacuo* at 45° C. to approximately 2 liters, the extract was centrifuged, and the residual solid collected, dried, and washed thoroughly with acetone to yield a yellowish-brown solid (11.7 g.). This product assayed 20,000 units/mg.; its ultraviolet absorption spectrum is given in Fig. 1.

Paper Chromatography

Ascending paper chromatography was carried out using strips of Whatman No. 1 filter paper in the following solvent systems:

A, water-saturated *n*-butanol.

B, water-saturated *n*-butanol on paper buffered with 0.1 *N* sodium carbonate.

C, water-saturated *n*-butanol on paper buffered with 0.1 *N* sodium phosphate, pH 12.0.

D, *t*-butanol-water (4:1).

E, *n*-butanol-ethyl acetate (1:1) saturated with water.

The samples were applied in 80% ethanolic solution, at several different concentrations so that on at least one chromatogram of each series a satisfactory zone for each active component was obtained. This was found to be necessary since too heavy applications caused streaking and elongated zones, and because of the differences in the amount of each component present in a particular complex, concentrations which were appropriate for one fraction were too low for the detection of the second.

After the chromatogram had been developed it was air dried and the position of active zones was determined by placing it on a plate of nutrient agar seeded with *Candida albicans*. The paper was removed after 2 hours and the dish incubated for 24 hours at 37° C. The results are given in Table I.

Countercurrent Distribution

The solvent system used was a mixture of ethyl acetate, *n*-propanol, and 0.1 *N* ammonium acetate buffer at pH 7.0 in the proportions 3:1:3. The antibiotic preparation (500 mg.) was dissolved in both phases (40 ml.) of the first tube and distributed to 60 transfers. The contents of all tubes were then removed and diluted with ethanol to 50 ml., when a homogeneous solution was obtained. The absorption spectrum between 250 and 400 m μ was measured with a recording spectrophotometer.

ACKNOWLEDGMENTS

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THE STRUCTURE OF BUTADIENE DIMERS PRODUCED BY A FREE-RADICAL CHAIN-TRANSFER MECHANISM¹

L. J. GENDRON² AND R. V. V. NICHOLLS

ABSTRACT

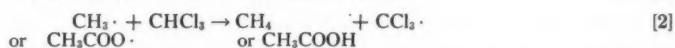
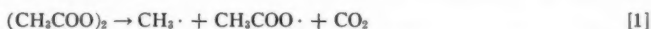
Butadiene was dimerized by using acetyl peroxide as source of free radicals and chloroform as solvent and chain-transfer agent. The dimers were identified and their structures were determined by means of ozonolysis and oxidative hydrolysis. It was established that two dimers were produced in nearly equal amount. One dimer was formed only by 1,4-additions, the other only by 1,2-additions. This result implies that polybutadienes may be mixtures of two varieties: one variety resulting from 1,4-additions, the other from 1,2-additions.

INTRODUCTION

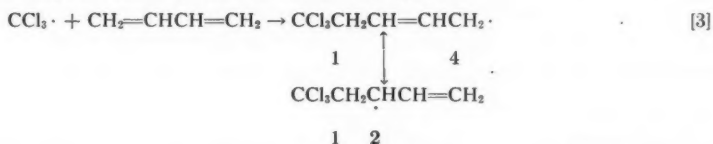
The amount of 1,2- and 1,4- units in polybutadienes has been determined by many investigators but the distribution of these units along the polymer chain is assumed to be at random. The aim of the present work is to gain more information about the validity of this assumption.

It was thought that the simplest polybutadienes, the dimers, would offer some interesting structural resemblances to their higher homologues and would be more readily dealt with. The dimers were produced by a free-radical mechanism in order to compare their structures with those of commercial polymers obtained by the same mechanism.

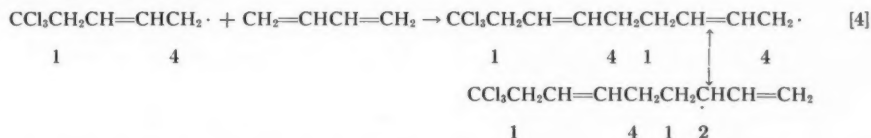
The following dimerization mechanism may be proposed when chloroform is used as chain-transfer solvent and acetyl peroxide as a source of free radicals. The peroxide breaks down into free methyl and acetyl radicals, which in turn liberate trichloromethyl radicals by reacting with chloroform.



The latter radicals, by attacking butadiene molecules at the terminal carbon atoms, form free trichloropentenyl radicals which are resonance hybrids:



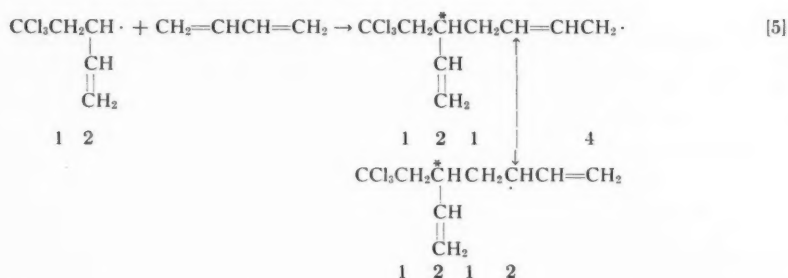
Each trichloropentenyl radical gives rise to trichlorononadienyl radicals by reacting with butadiene molecules:



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Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Quebec, with financial assistance from the National Research Council.

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Each free trichlorononadienyl radical then becomes a stable dimer molecule by extracting a hydrogen atom from a chloroform molecule, thus producing a new free trichloromethyl radical which may repeat the same process (Reaction 3).

Four dimers, isomers of trichlorononadiene, may be obtained according to the mode of addition of butadiene. The first two are straight-chain molecules (Reaction 4). Since each of the last two isomers (Reaction 5) has an asymmetric (*) carbon atom, four optical isomers are possible.

EXPERIMENTAL AND RESULTS

Synthesis of the Dimers

After many lengthy trials, appropriate experimental conditions were devised and the following procedure was adopted. A solution containing 18.5 g. of butadiene (0.34 mole) and 20 g. of acetyl peroxide (0.17 mole) in 4000 g. of chloroform (33.5 moles) was maintained at 50° C. during 7 days. At the end of this period, the chloroform was expelled by distillation *in vacuo* at room temperature until the volume of the solution had been reduced to 200 ml. The solution was then treated with an aqueous solution of ferrous sulphate to destroy any residual peroxide, washed with water, and dried with anhydrous sodium sulphate. The remaining chloroform was removed *in vacuo* leaving a residue of 19.9 g. (yield: 51%, calculated as trichlorononadiene).

This residue was a yellow liquid with a fishy odor (several people identified the odor as that of cod liver or whale oil). When a freshly-prepared sample was heated above 50° C., it evolved hydrogen chloride. No boiling occurred when it was submitted to a vacuum of 10 μ at room temperature. It was not further purified.

Identification of the Dimers

The identification of the residue as butadiene dimer or dimers is based on the data shown in Table I.

The results of elemental analysis and molecular-weight determination agree with the calculated values. The molar refraction is lower than that calculated by 1.9 unit; this lower value is not unreasonable if one considers that the additivity of constant increments for each typical bond is not strictly valid and that differences have been observed between isomers (21).

The ultraviolet spectrogram (Fig. 1) revealed the absence of conjugated carbon-carbon double bonds as was expected. The structural configuration $\text{RCH}=\text{CHR}'$, which indicates a 1,4-addition, and the $\text{RCH}=\text{CH}_2$ configuration, which denotes a 1,2-addition, were identified by infrared spectroscopy (Fig. 2). Methyl groups, indicating a terminal 1,4-addition, and carbon-chlorine bonds were also identified. However, the presence of carbonyl groups in trace amounts was unexpected. The presence of carbonyl

TABLE I
 IDENTIFICATION OF DIMERS

	Calculated or expected	Found
%Cl	46.5	46.7
%C	47.5	47.5
%H	5.75	5.59
Molecular weight	227.6	227
Specific gravity at 25° C.	—	1.214
Refraction index n_D^{25}	—	1.5061
Molar refraction	57.3	55.4
Ultraviolet spectrogram	No conjugated C=C bonds	No conjugated C=C bonds
Infrared spectrogram	RCH=CHR' <i>cis</i>	Yes
	RCH=CHR' <i>trans</i>	Yes
	RCH=CH ₂	Yes
	—CH ₃ groups	Yes
	C—Cl bonds	Yes
	No C=O groups	Traces
Iodine number (Wijs method)	223	152
(modified method)	223	168
(modified method)	223	208
Optical activity	—	None
Urea complex formation	—	None

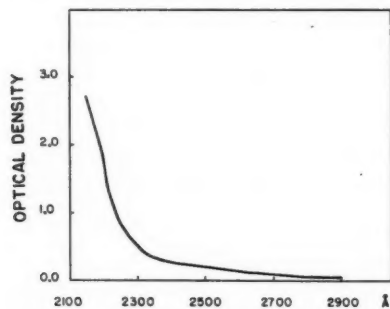


FIG. 1. Ultraviolet spectrogram of dimers.

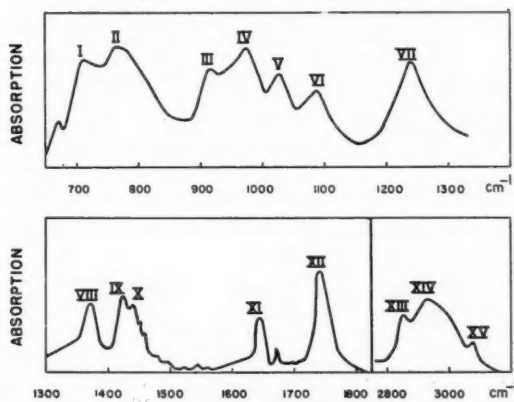


FIG. 2. Infrared spectrogram of dimers.

groups may have resulted from a reaction between free acetyl radicals and butadiene molecules, the reaction products not being eliminated completely during the purification of the dimers.

The iodine number 152 determined by the Wijs method (16) was low. A value of 168 was found when the reaction time was increased from 30 to 60 minutes and a value of 208 was obtained when the concentration of chlorine was increased to five times the concentration of iodine, the reaction time being 30 minutes. Faragher, Gruse, and Garner (6), von Mikusch and Frazier (17), and Rehner (20) have established that the addition of iodine monochloride to ethylenic compounds gave unpredictable results. Thus, the experimental conditions for iodine monochloride addition have had to be modified repeatedly in order to obtain the expected degree of unsaturation in natural and synthetic rubbers (9, 10, 12, 20).

No optical activity was found although optical isomers were possible. However, their formation is not excluded since optical isomers are usually produced in equimolar amounts.

Urea is known to form insoluble complexes with normal alkanes and alkenes (18, 23) but when the dimers were treated with this reagent, no precipitate was obtained. This negative result is not a proof that straight-chain dimers were not formed; it is probable that the three chlorine atoms, even though they are on a terminal carbon atom, prohibit urea-complex formation (23).

Structure of the Dimers

A quantitative discrimination between each of the four isomer dimers is possible by determining the amounts of succinic, acetic, and formic acids produced by ozonolysis

TABLE II
ACIDS OBTAINABLE FROM DIMERS BY OZONOLYSIS AND OXIDATIVE HYDROLYSIS

(A) $\text{CCl}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$ 1 4 1 4	→ $\text{CCl}_3\text{CH}_2\text{COOH}$ + $\text{HOOCCH}_2\text{CH}_2\text{COOH}$ + CH_3COOH
(B) $\text{CCl}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ 1 4 1 2	→ $\text{CCl}_3\text{CH}_2\text{COOH}$ + $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ + HCOOH
(C) $\text{CCl}_3\text{CH}_2\text{CHCH}_2\text{CH}=\text{CHCH}_3$ $\begin{array}{c} \text{CH} \\ \\ \text{CH}_2 \end{array}$ 1 2 1 4	→ $\text{CCl}_3\text{CH}_2\text{CHCH}_2\text{COOH}$ $\begin{array}{c} \text{COOH} \end{array}$ + CH_3COOH + HCOOH
(D) $\text{CCl}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ $\begin{array}{c} \text{CH} \\ \\ \text{CH}_2 \end{array}$ 1 2 1 2	→ $\text{CCl}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{COOH}$ $\begin{array}{c} \text{COOH} \end{array}$ + 2 HCOOH

and oxidative hydrolysis of the dimers (Table II). Succinic acid would be formed only from dimer A. Acetic acid would be obtained from dimer A and dimer C, one mole from each mole of dimers A and C. Formic acid would be formed from dimer B and dimer D, dimer B giving one mole and dimer D two moles.

The dimers were treated with ozone and the resulting ozonides decomposed with hydrogen peroxide. The yield of organic acids was between 70 and 80%, depending on the experimental conditions, such as temperature of ozonolysis and excess of ozone. This yield agrees well with those obtained by Alekseeva (1), Rabjohn (19), and Marvel (14). The organic acids were separated by partition chromatography on a silica-gel column according to the technique developed by Marvel and Rands (13), and improved by Bulen, Varner, and Burrell (5). The chromatogram of the total acids is shown in Fig. 3. Two other chromatograms were obtained when the total acids were separated into volatile and non-volatile fractions.

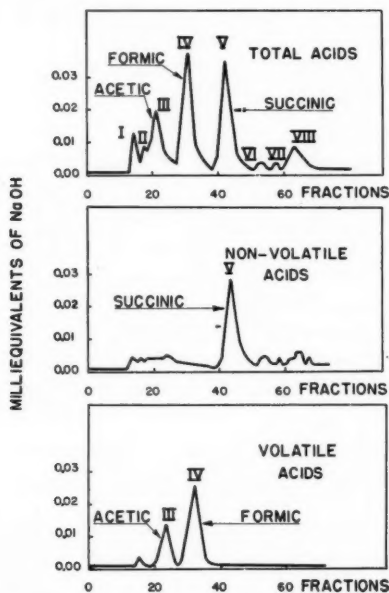


FIG. 3. Chromatograms of the acids obtained by hydrolysis of dimer ozonides.

Peak V in the total-acids chromatogram was reproduced at the same eluant fraction in the non-volatile acids chromatogram; the acid corresponding to this peak was identified as succinic acid. Peaks III and IV in the total-acids chromatogram occurred at the same eluant fractions in the volatile-acids chromatogram; the acids corresponding to these peaks were identified as acetic and formic acids, respectively.

The acids corresponding to peaks I and II contained chlorine; they were assumed to be mainly 3,3,3-trichloropropionic acid and (2,2,2-trichloroethyl)-2-glutaric acid or fragments of these. The 3,3,3-trichloropropionic acid hydrolyzes very easily according to Brown and Musgrave (4) and the (2,2,2-trichloroethyl)-2-glutaric acid seems to be unknown. The acids corresponding to peaks VI, VII, and VIII did not contain chlorine; they were assumed to be other hydrolysis products of the chlorinated acids.

The amounts of succinic, acetic, and formic acids were evaluated from the chromatograms; these were 0.45 mole, 0.44 mole, and 1.0 mole respectively, on a basis of one mole of dimer.

Since only dimer A gives succinic acid and since one mole of dimer A gives one mole of succinic acid, it is concluded that the mole fraction of dimer A is 0.45. Since the formation of acetic acid is equal to the formation of succinic acid, all of the acetic acid comes from dimer A. Thus, dimer C is not produced; otherwise the experimental value for acetic acid should be higher than that of succinic acid. If the remaining mole fraction, 0.55 mole, is the dimer D, it should yield 2×0.55 mole of formic acid; experimentally 1.0 mole of formic acid was determined, showing that the remaining mole fraction is mostly dimer D (0.45 mole) and a lesser quantity of dimer B (0.10 mole).

Dimers A and D were obtained in equal amounts, 45% of each. Consequently, when butadiene is dimerized by a free-radical chain-transfer mechanism, if the initial step is a 1,4-addition, the second step is also a 1,4-addition as in the case of dimer A; if, on the other hand, the initial step is a 1,2-addition, the second step is also a 1,2-addition as in the case of dimer D.

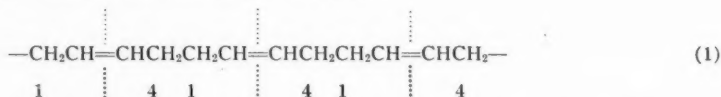
GENERAL DISCUSSION

These results are in agreement with those obtained by Kharasch (11), who observed that when *tert*-butyl hydroperoxide is decomposed by traces of cobalt salts in the presence of butadiene, nearly equal amounts of 1,2- and 1,4-addition products are produced. These results also confirm the work of Hart and Meyer (7), who found that the heat and entropy of activation favor only slightly 1,4-addition over 1,2-addition.

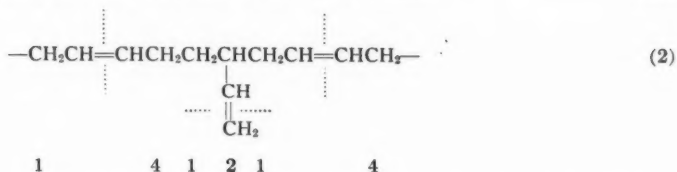
However, in polybutadienes the percentage of 1,2-addition is not 50% as was found in our dimers, but only 20%. This discrepancy could be explained by the fact that, in dimers, the predominating steps are the initiation and termination of the chains, whereas, in polymers, the predominating step is the propagation of the chains. Alfrey, Bohrer, and Mark (3) state that a greater propagation rate for 1,4-addition over 1,2-addition can be ascribed to a steric effect.

The most striking fact is that the second step of the dimerization is like the initial step, a 1,4-addition when the initial step is a 1,4-addition and a 1,2-addition when the initial step is a 1,2-addition. If these results are extrapolated to polybutadienes, two other varieties of polybutadienes should be found along with the conjunctive 1,2- and 1,4-variety, one variety produced exclusively by 1,2-additions and the other variety produced exclusively by 1,4-additions. This prediction, enunciated by Hill, Lewis, and Simonsen (8), has not as yet received direct experimental support. However, our calculations, based on the results obtained by several investigators, show that independent varieties of polybutadienes may be found.

Marvel (15) showed that polybutadienes of different conversions gave large amounts of succinic acid and small amounts of 1,2,4-butanetricarboxylic acid; succinic acid can result only from adjacent 1,4-additions (Structure (1)):

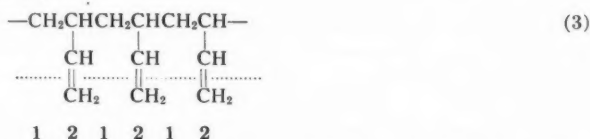


On the other hand, 1,2,4-butanetricarboxylic acid can be formed only from a structural unit in which a 1,2-addition occurs between two 1,4-additions (Structure (2)):



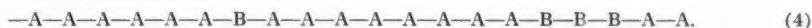
Taking into account that 20% of the butadiene polymerizes according to a 1,2-addition, and if each of these 1,2-additions occurs between two 1,4-additions, the resulting polybutadiene will give, under ozonolysis, a (succinic acid)/(1,2,4-butanetricarboxylic acid) ratio equal to 3 on a mole basis. From the results of Marvel (15) we calculated this ratio to be about 14 for many polybutadienes. For butadiene-*o*-chlorostyrene (14) and butadiene-styrene (15) copolymers, the ratios were 8 and 5, respectively.

A ratio higher than 3 may be explained only by the formation of adjacent 1,2-additions in the polymers (Structure (3)):



When adjacent 1,2-additions take place, less 1,2-units are available to form the structural unit (2) and more 1,4-units are available to become adjacent (Structure (1)). A ratio of 14 implies that most of the 1,4-additions are grouped together and consequently most of the 1,2-additions are also grouped together.

This implication is not a proof that independent varieties of polybutadienes are really produced during polymerization since long sequences of 1,4-additions and 1,2-additions may be distributed along the same chain. For instance, structural unit (4), where the 16 1,4-addition units are represented by A and the four 1,2-addition units by B, gives a ratio of 14 under ozonolysis:



Structural unit (4) resembles a copolymer chain where A and B are different monomers. The butadiene, before reaction, is a single species but, at the instant of its reaction or activation, it behaves like two monomers. Well, Powers, Sands, and Stent (22) have already set forth a somewhat similar opinion. On the other hand, Alfrey, Bohrer, and Mark (2) established that long sequences of the same units along the copolymer chain are remotely probable from a mathematical standpoint. Short sequences of each unit along the copolymer chain are obtained if the free-radical growing chain, whatever be the nature of the ending unit, has the aptitude to react, nearly as well with one monomer as with the other. It seems that butadiene has not this aptitude since nearly all the dimers are formed only by adjacent 1,4-additions or adjacent 1,2-additions, even though the over-all percentage of 1,2-additions is 50% instead of 20% as in polymers. It follows that the probability of finding independent varieties of polybutadienes is relatively high.

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THE ACTION OF Co^{60} GAMMA RAYS AND OF FENTON'S REAGENT ON AQUEOUS BROMAL HYDRATE SOLUTIONS¹

R. J. WOODS AND J. W. T. SPINKS

ABSTRACT

Aqueous bromal hydrate solutions have been irradiated with Co^{60} gamma rays and the production of acid measured. The effect of bromal hydrate concentration, dose rate, pH, and temperature upon the yield of acid has been determined. Major products of the radiolysis have been identified and are compared with those formed when aqueous bromal hydrate solutions are treated with Fenton's reagent, a mixture of hydrogen peroxide and ferrous sulphate solutions. It has been shown that Fenton's reagent will initiate a chain reaction in aqueous bromal hydrate solutions which produces hydrobromic acid.

INTRODUCTION

Organic halogen compounds are among the substances most sensitive to ionizing radiation, the corresponding hydrogen halide frequently being formed in comparatively high yield. These strong acids may readily be determined and their formation offers a convenient means of studying the radiolysis of the parent compound under various conditions.

Chloral hydrate, $\text{Cl}_3\text{C} \cdot \text{CH}(\text{OH})_2$, and its halogen analogues are particularly suitable for study in this manner because of their high solubility in water, and previous publications from this laboratory have dealt with the irradiation of chloral hydrate (2, 3). The present paper describes experiments in which bromal hydrate, $\text{Br}_3\text{C} \cdot \text{CH}(\text{OH})_2$, has been irradiated in aqueous solution with the gamma rays from cobalt-60. The effect of bromal hydrate concentration, dose rate, pH, and temperature upon the yield of acid from air-saturated solutions has been determined.

Major products formed in bromal hydrate solutions by Co^{60} gamma irradiation have been identified. The reaction brought about by gamma rays has been compared with that initiated by Fenton's reagent.

EXPERIMENTAL

Bromal Hydrate

Bromal hydrate was prepared by stirring 200 g. bromal (Eastman Kodak, b.p. 71–74° at 118 mm.) with 70 ml. water until the mixture was homogeneous, cooling, and filtering off the crystalline hydrate. The product was crystallized to constant melting point from a small quantity of water, using water which had been distilled from alkaline permanganate and redistilled from an alkaline suspension of manganous hydroxide. The crystals were dried over phosphorus pentoxide; melting point after drying, 54.5° C. Semimicro analysis by treatment with standard alkali and back titration with standard acid (cf. Ref. 8) gave a value of 102% $\text{Br}_3\text{C} \cdot \text{CH}(\text{OH})_2$. A sample of the crystalline hydrate which had been air-dried overnight also had an apparent purity of 102%, determined by the same method. Thus, it appears that the crystals rapidly lose the molecule of water of crystallization with which they crystallize (6).

Occasionally crystallization of bromal hydrate, m.p. 54–55° C., gave material of m.p. 73° C. The higher melting crystals gave the same yield of acid upon irradiation as the material of m.p. 54.5° C. and after they had been left for several months, or upon

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further crystallization, reverted to material of m.p. 54–55° C., identical (mixed melting point, analysis as above, acid yield upon irradiation) with the bromal hydrate normally obtained. The higher melting crystals were not analyzed but appear to be a second crystalline form of bromal hydrate. Pope (6) described the dimorphism of chloral hydrate but was unable to prepare a second form of bromal hydrate; Wolf (10) disputes Pope's claim to have isolated two forms of chloral hydrate.

Quantitative Irradiations

Irradiations were carried out using Co^{60} sources of about 1 and 700 curies, respectively (7). Dose rates were measured using a Victoreen condenser r-meter, Model 70, corrected for Co^{60} radiation (5) or by determining the ferric ion formed (9) on irradiating solutions of ferrous ammonium sulphate. In the latter case a G value of 15.5 for the formation of ferric ions was used and a conversion factor of 1 roentgen = 0.975 rad (4). Dose rates which were determined by both procedures agreed to better than 2%.

Solutions were made up in water that had been distilled from alkaline permanganate and then redistilled from an alkaline suspension of manganous hydroxide. Glassware was cleaned by allowing it to stand several hours in a fresh solution of chromic acid in concentrated sulphuric acid followed by thorough rinsing with water, distilled water, and the specially distilled water. Solutions were generally prepared immediately before use; bromal hydrate solutions which had been kept more than about a week gave a lower yield of acid on irradiation.

Aliquots of 2.0 or 3.0 ml. were irradiated in stoppered test tubes, 13×100 mm., contained in wells 40 mm. deep in a lucite block, or immersed in a water bath and then titrated as soon as possible. The acid formed was titrated with approximately 0.1 N sodium hydroxide solution after two drops of a 0.1% solution of bromophenol blue in aqueous ethanol had been added. Sodium hydroxide was added until the color of the solution reached that of a non-irradiated aliquot containing an equal amount of indicator. It was necessary to add a small, measured amount of the standard alkali to non-irradiated aliquots of the more concentrated solutions of bromal hydrate to bring these solutions to the faint blue color convenient for comparison. The solutions were viewed with artificial (tungsten) light. Bromide in the irradiated solution was determined by titration with 0.01 N silver nitrate solution using three drops of a 0.01% aqueous solution of the sodium salt of eosin as indicator. No bromide could be detected by this method in non-irradiated solutions. Titrations were carried out in the irradiated test tubes after inserting a small motor-driven stirrer and the tip of a microburette. Titration of aliquots irradiated in individual tubes gave values which sometimes varied from the average value for a number of such tubes by as much as 5%. However, non-irradiated solutions containing 1 to 10 microequivalents of standard hydrobromic acid could be titrated with an accuracy of 1%, or better. The average of at least three individual titrations was taken for each point as in Fig. 1. Yields, in terms of microequivalents per liter per kiloroentgen, were determined by plotting the experimental results, as shown in Fig. 1, and measuring the slope of the line.

To titrate the acid formed in aqueous bromal hydrate solutions with alkali, it is necessary to use an indicator such that the final solution will be at a pH less than about 6; solutions of higher pH rapidly decompose bromal into bromoform and a formate.

An experiment in which some of the irradiated samples were titrated with alkali immediately and others after storing in the dark for 24 and 80 hours, respectively, showed no change in the titration value after 24 hours and only a slight change after 80 hours.

The irradiated solutions contained no materials capable of oxidizing starch-iodide paper.

2,4-Dinitrophenylhydrazones of the Bromoacetaldehydes

With a solution of 2,4-dinitrophenylhydrazine sulphate in methanol, bromal gave a bromine-containing derivative which crystallized from glacial acetic acid as an orange powder, m.p. 267° C. (decomp.). A small quantity of a second derivative was isolated from the mother liquors; bronze-red needles from aqueous ethanol, m.p. 129° C.

Dibromoacetaldehyde gave a derivative crystallizing as orange-yellow needles from a mixture of benzene and light petroleum (Skelly F), m.p. 146° C., if the aldehyde was in excess. If an excess of 2,4-dinitrophenylhydrazine sulphate was used, the major product was a halogen-free derivative, m.p. 327° C. (decomp.). The melting point was not changed after admixture with the bis-2,4-dinitrophenylhydrazone of glyoxal, m.p. 326° C. (decomp.).

Monobromoacetaldehyde, in excess, gave a product crystallizing as orange needles from a mixture of ethyl acetate and methanol, m.p. 148° C. With an excess of reagent only the bis-2,4-dinitrophenylhydrazone of glyoxal could be isolated.

Irradiation of Aqueous Bromal Solution, Identification of Products

A solution of bromal hydrate (48 g.) in water (80 ml.) was irradiated with cobalt-60 gamma rays (1.3×10^5 r./hour; total dose, 5×10^6 r.). During the irradiation, a slow stream of oxygen was bubbled through the solution and then through a solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid; a very small quantity of an orange derivative, m.p. 305–310° C. (decomp.) separated.

After irradiation the solution contained 38 milliequivalents of bromide ion and 42.5 milliequivalents of acid (determined by titration with sodium hydroxide).

When cooled in an ice-bath the irradiated solution deposited white crystals, which were filtered off, washed with a little cold water, and dried; the dried crystals (19.6 g.) analyzed as 100% bromal hydrate. The combined filtrate and wash-liquor were continuously extracted with ether overnight, and then the ether extract stirred with a suspension of 3 g. calcium carbonate in 40 ml. water. The ether layer was separated and the aqueous residue continuously extracted with a further quantity of ether. The combined ethereal solutions were dried overnight over magnesium sulphate, filtered, evaporated, and distilled through a short fractionating column. Two fractions, b.p. 104° C. (1.05 g.) and b.p. 162–164° C. (20 g.), were obtained. With 2,4-dinitrophenylhydrazine sulphate the material of b.p. 104° C. gave dibromoacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 147° C., and the bis-2,4-dinitrophenylhydrazone of glyoxal, m.p. 328° C. (decomp.); the melting points were undepressed on admixture with authentic specimens. The fraction of b.p. 162–164° C. formed a 2,4-dinitrophenylhydrazone crystallizing as orange needles from glacial acetic acid, melting point alone and after admixture with bromal 2,4-dinitrophenylhydrazone, 263° C. (decomp.). Assuming this fraction to be recovered bromal, an estimation of the purity by the method described above gave a value of 116%. Under these conditions bromal acts as a monobasic acid and dibromoacetaldehyde as a tribasic acid; thus the high value would be explained if the bromal contained about 6% of dibromoacetaldehyde. The bulk of the bromal was recovered as the crystalline hydrate after a little water was added to the fraction.

The aqueous calcium carbonate suspension was acidified with hydrochloric acid, extracted with ether, and the extract dried over magnesium sulphate, filtered, and evaporated. The residue (345 mg.) was dissolved in a little cold sodium hydroxide solution and

allowed to stand a few minutes, in order to decompose any bromoacetaldehydes present, then acidified, and evaporated. Distillation of the residue, under vacuum, gave a small quantity of colorless oil (equiv. wt. 216; calc. for $\text{Br}_2\text{CH.COOH}$, 218). The infrared spectrum of the oil was identical with that of an authentic specimen of dibromoacetic acid.

Thus, it appears that the major products formed by the irradiation of an aqueous bromal solution are hydrobromic acid, dibromoacetaldehyde, and dibromoacetic acid.

Fenton's Reagent on Bromal Solutions, Identification of Products

Bromal hydrate (32.8 g., 0.11 mole) was dissolved in 200 ml. water, and solutions of ferrous sulphate (93 g. in 165 ml. water, 0.33 mole) and hydrogen peroxide (39 ml. of 29% solution diluted to 165 ml. with water, 0.33 mole) were added dropwise and with stirring. The two solutions were added simultaneously and at about the same rate, so that the total addition took 3 hours. When the addition was complete, the solution contained 85 milliequivalents of bromide ion.

The mixture was extracted with ether for 48 hours and the ether extract divided into neutral and acid fractions as described above. Distillation of the neutral fraction (18 g.) gave fractions of b.p. 110–120° C. (5.85 g.) and b.p. 160–170° C. (5.1 g.) and a tarry residue (about 1 g.) from which no volatile material could be obtained by vacuum distillation. The material of b.p. 110–120° C. gave a 2,4-dinitrophenylhydrazone of m.p. 147° C., unchanged by admixture with the 2,4-dinitrophenylhydrazone of dibromoacetaldehyde but depressed to 124° C. by admixture with the derivative from monobromoacetaldehyde (m.p. 148° C.). The bis-2,4-dinitrophenylhydrazone of glyoxal, m.p. and mixed m.p. 329° C. (decomp.), was also obtained. The fraction of b.p. 160–170° C. gave bromal 2,4-dinitrophenylhydrazone, m.p. 266° C. (decomp.), unchanged by admixture with an authentic specimen. An estimation of the purity of the fraction, regarding it as recovered bromal, gave an apparent value of 141%, suggesting that it still contained about 13% of dibromoacetaldehyde.

The crude acid fraction (4.65 g., m.p. 70° C., equiv. wt. 308 by direct titration with alkali or 285 by treatment with an excess of alkali and back titration with acid) was dissolved in a little cold 2 *N* sodium hydroxide solution and allowed to stand a few minutes, acidified, and evaporated. The organic acid was recovered by sublimation from the residue (at 95° C. and 1 mm.) and crystallized from a mixture of benzene and Skelly F to give tribromoacetic acid as large, flat needles, m.p. 126° C., unchanged by admixture with authentic tribromoacetic acid, m.p. 126.5° C. The infrared spectrum of the recovered acid was identical with that of authentic tribromoacetic acid; dibromoacetic acid and tribromoacetic acid may be readily distinguished by means of their infrared spectra.

Thus the major products formed when Fenton's reagent reacts with bromal appear to be hydrobromic acid, dibromoacetaldehyde, and tribromoacetic acid.

Fenton's Reagent on Bromal Solutions, Quantitative Experiments

Measured volumes of standardized hydrogen peroxide solution were added to aliquots of bromal hydrate solution (5.0 ml. of 0.34 *M*) and sufficient water to bring the volume of the mixture to 10.0 ml. While stirring, 1.0 ml. of ferrous sulphate solution (0.1 *M*) was pipetted into the mixture, and then the stirring was continued for several minutes. Aliquots of the mixture (2.0 ml.) were titrated with silver nitrate solution using eosin as indicator; if necessary, a drop of dilute acetic acid was added just before titrating to give a clear solution.

RESULTS

Irradiation of Bromal Hydrate Solutions, Quantitative Results

Results obtained in a typical irradiation of an aqueous bromal hydrate solution are shown in Fig. 1. The graph is similar to those obtained when aqueous solutions of chloral

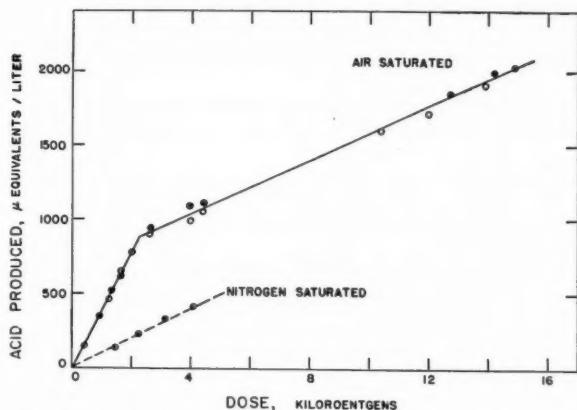


FIG. 1. Acid produced on irradiation of 0.15 molar bromal hydrate solution at a dose rate of 11 roentgens/minute.

- total acid, titrated with sodium hydroxide solution to pH 4.
- hydrobromic acid, titrated with silver nitrate solution.
- ⊙ total acid, nitrogen saturated solutions.

hydrate were irradiated, and by analogy with the results obtained by Freeman, Van Cleave, and Spinks (2) the break in the curve is correlated with exhaustion of the oxygen originally present in the solution. This was confirmed in the present instance by irradiating a solution through which nitrogen had been bubbled to displace dissolved oxygen. The results obtained are shown by the broken line in Fig. 1, which is parallel with the second part of the curve. The break in the curve occurred when between 700 and 900 microequivalents per liter of acid had been formed and, within these limits, was independent of concentration, dose rate, or pH. Water would contain about 260 micromoles per liter of dissolved oxygen under the conditions of the experiments.

The acid formed was normally titrated with dilute alkali, but Fig. 1 also shows points corresponding to the radiation-liberated bromide in the solution. The close correspondence between the two groups suggests that hydrogen bromide is the major acidic product.

In the course of this work a number of batches of bromal hydrate were prepared, all crystallized to constant melting point, and all apparently identical. However, the yield of acid varied when material from each batch was irradiated under standard conditions; extreme values for the yield of acid when 0.15 molar solutions were irradiated at 22° C. and at a dose rate of 10 r./minute were 440 and 790 microequivalents of acid per liter per kiloroentgen. The differences can probably be attributed to traces of acid which were not completely removed by crystallization; small pH changes in the region 4.5 to 6 appear to have a large effect on the yield of acid obtained by irradiation (cf. Table III). Use of material from a single batch gave reproducible results, and the effect of the variables concentration, dose rate, and temperature was determined using one sample

of bromal hydrate throughout. The relationship between yield and, for example, dose rate was found to be the same when several samples of bromal hydrate, each giving different yields, were tested.

The effect of variations in temperature on the yield of acid is shown in Table I. Irradiations were carried out at $22 \pm 3^\circ \text{C}$. and corrected to 22°C . using a temperature coefficient of 3.5% per degree centigrade (based on the yield at 22°C .).

The variation in the amount of acid formed per kiloroentgen with changes in the molarity of the bromal hydrate solution is shown in Fig. 2. The two curves, A and B,

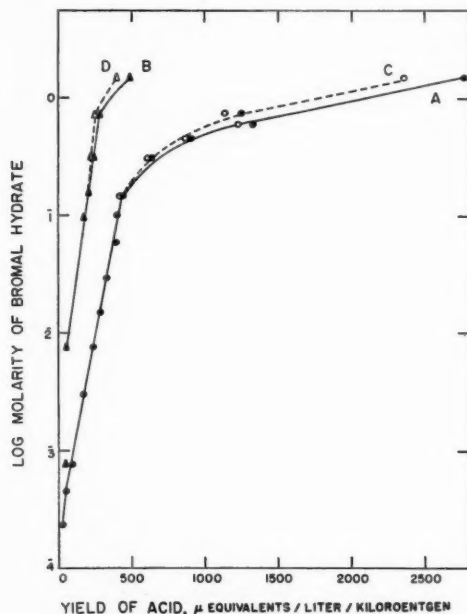


FIG. 2. Effect of concentration. Irradiation of aqueous bromal hydrate solutions at a dose rate of 11 roentgens/minute. The scale for the G values, shown by the broken lines, is the same as that for the yield of acid but the units are molecules of monobasic acid formed/100 ev. of energy absorbed.

correspond to the acid yield before the oxygen present in the solution is used up, and the yield after this point is reached, respectively.

TABLE I
VARIATION IN ACID YIELD WITH TEMPERATURE
(0.15 molar bromal hydrate solutions, 20 r./min.)

Temperature ($^\circ \text{C}$.)	Yield ($\mu\text{eq.}/\text{l.}/\text{kr.}$)
28	474
22	373
20	348
4.5	139
3	137

Calculation of G Values

The factor to convert the yield of acid in microequivalents per liter per kiloroentgen

to the G value for the production of acid, i.e., the number of molecules of monobasic acid formed per 100 electron volts of energy absorbed, was obtained in the following manner.

Bromal hydrate (mol. wt. 299) and water contain $0.455 \times 6 \times 10^{23}$ and $0.555 \times 6 \times 10^{23}$ electrons per gram, respectively. Thus, the relative number of electrons per gram for a M molar solution of bromal hydrate compared to water will be

$$[1] \quad \frac{M(299)(0.455) + (1000d - 299M)(0.555)}{1000(0.555)d} = \frac{d - 0.054M}{d},$$

where d is the density of the M molar bromal hydrate solution. Using the expression given by Gray (4) to relate the absorbed dose in water to a dose of cobalt-60 gamma radiation of 1 roentgen,

$$\begin{aligned} 1 \text{ roentgen} &\equiv 0.975(W/34) \text{ rad} \\ &\equiv 0.975(W/34)(100) \text{ ergs/gram.} \end{aligned}$$

Taking W equal to 34 electron volts per ion pair in air, this becomes

$$\begin{aligned} 1 \text{ roentgen} &\equiv 97.5 \text{ ergs/gram water} \\ &\equiv 6.08 \times 10^{13} \text{ electron volts/gram water.} \end{aligned}$$

Since absorption of cobalt-60 gamma radiation will be by the Compton process, the energy absorption of solutions other than pure water may be obtained from this expression by correcting for the relative number of electrons per gram of the solution. For a M molar bromal hydrate solution, using the relationship [1], the energy absorption per roentgen becomes

$$1 \text{ roentgen} \equiv 6.08 \times 10^{13}(d - 0.054M)/d \text{ ev./gram solution}$$

and $1 \text{ kiloroentgen} \equiv 6.08 \times 10^{16}(d - 0.054M)(1000d)/d \text{ ev./liter solution.}$

Substituting for roentgens in

$1 \mu\text{eq./liter/kiloroentgen} \equiv 6.02 \times 10^{17} \text{ molecules*/liter/kiloroentgen}$
this becomes

$$[2] \quad 1 \mu\text{eq./liter/kiloroentgen} \equiv 6.02 \times 10^{17} / [6.08 \times 10^{16}(d - 0.054M)(1000)] \text{ molecules/ev.} \\ \equiv \{1 / [(1.01)(d - 0.054M)]\} G, \text{ the units of the } G \text{ value being molecules/100 ev.}$$

TABLE II
DENSITY OF BROMAL HYDRATE SOLUTIONS AT 22.5° C. AND FACTOR TO
CONVERT MICROEQUIVALENTS/LITER/KILORENTEGEN TO G VALUES

Molarity	Density (g./ml.)	Conversion factor
2	1.370	0.78
1	1.187	0.87
0.6	1.094	0.93
0.2	1.035	0.97
0.06	1.010	0.98
0.01	0.999	0.99

Table II shows the density of bromal hydrate solutions at 22.5° C. and values of the conversion factor calculated from expression [2].

G values calculated according to the foregoing procedure are plotted in Fig. 2 as

*Of monobasic acid.

curves C and D; at low concentrations curves A and C and curves B and D coincide. The magnitudes of the yields of acid are such that a chain mechanism must be postulated to explain them.

Effect of Dose Rate on Yield

In Fig. 3 is shown the effect of dose rate on the yield of acid per kiloroentgen obtained from air-saturated 0.15 molar bromal hydrate solutions. The yield is apparently inversely

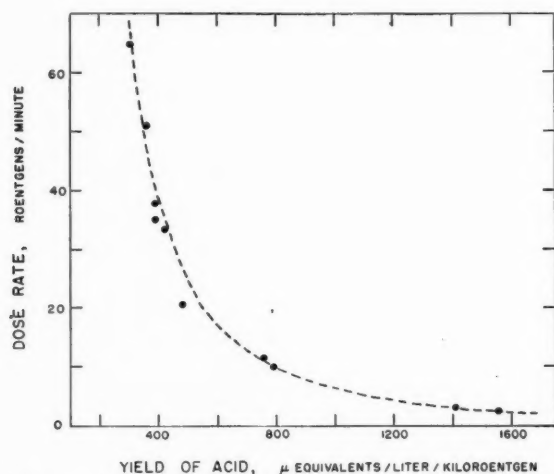


FIG. 3. Effect of dose rate. Irradiation of 0.15 molar aqueous bromal hydrate solution. Broken line corresponds to yields which would be expected if yield were inversely proportional to the square root of the dose rate.

proportional to the square root of the dose rate; the broken line corresponds to the yields expected if this relationship holds, taking the yield at a dose rate of 9.8 r./minute as standard.

Effect of pH on Yield

Table III shows the yields of acid obtained by irradiating a bromal hydrate solution to which a little acid or alkali had been added to alter the initial pH; the original solution had a pH of 4.5. The experimental results were plotted and in each case gave a graph similar to that shown in Fig. 1. Since, even at the highest pH used, the points obtained lay along a straight line, it was concluded that little change in pH occurred during the irradiations. A small amount of bromide was formed by hydrolysis in the solution at

TABLE III
EFFECT OF pH ON YIELD OF ACID PRODUCED BY IRRADIATION
(0.2 molar bromal hydrate solution, 9.8 r./min., 22° C.)

Initial pH	Acid produced (μeq. HBr/l./kr.)	
	Oxygen present	Oxygen exhausted
6	1950	228
4.5	655	145
2	620	155

pH 6. The values given in the table have been corrected for this. The results suggest that reproducible yields of acid might be assured by adjusting the pH of bromal solutions to between 2 and 4 before irradiation.

Effect of a Large Dose on a Dilute Bromal Solution

In Table IV are tabulated the quantities of acid formed when a dilute solution of bromal hydrate was irradiated with a sufficiently large dose of cobalt-60 gamma radiation that all of the bromal hydrate might be expected to be changed. From the results it is

TABLE IV
ACID FORMED ON IRRADIATION OF A 10^{-3} MOLAR SOLUTION OF BROMAL HYDRATE

Approx. dose (kr.)	Equiv. acid formed/mole bromal present	
	HBr (titrated with AgNO_3)	Total acid (titrated with NaOH)
32	1.45	1.45
65	2.15	2.15
100	2.55	2.5
160	2.75	2.7
320	2.95	2.9

concluded that a sufficiently large dose of radiation will convert all the bromine present to hydrobromic acid. All of the acid formed can be accounted for as hydrogen bromide though the products may include a very weak acid, e.g., carbonic acid, which would not be detected by titrating to pH 4. Under the conditions of this particular experiment, the intermediate build-up of an appreciable quantity of other acid also appears unlikely.

Fenton's Reagent on Bromal Solutions, Quantitative Results

Fig. 4 shows the yield of hydrobromic acid produced by adding small quantities of hydrogen peroxide solution to a solution of bromal hydrate which contained ferrous sulphate. It appears that the hydrobromic acid is produced by a chain mechanism

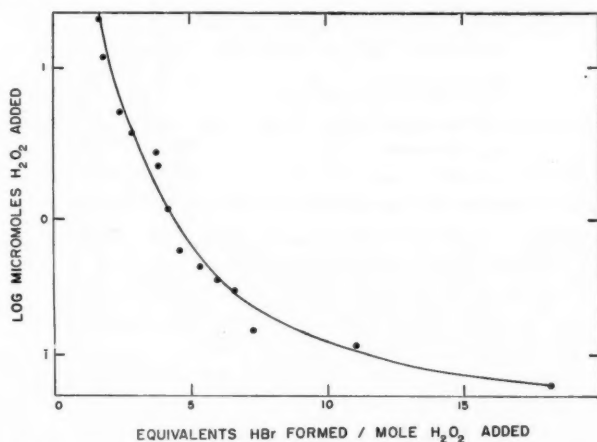


FIG. 4. Action of Fenton's reagent on bromal hydrate. Hydrobromic acid produced by adding hydrogen peroxide to an aqueous solution of bromal hydrate containing ferrous sulphate.

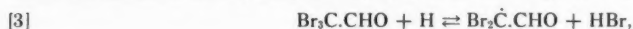
since each molecule of hydrogen peroxide added leads to the formation of several molecules of acid. The chain length is increased as the additions of hydrogen peroxide are made smaller.

DISCUSSION

The foregoing has indicated that the radiolysis of bromal in aqueous solution, in the presence of oxygen, is a chain reaction resulting in the formation of hydrogen bromide and dibromoacetaldehyde as major products and, to a smaller extent, dibromoacetic acid.

It is generally accepted that the primary action of ionizing radiation on dilute aqueous solutions results in the formation of hydrogen atoms and hydroxyl radicals which, with other reactive species derived from them, are largely responsible for the chemical effects observed. These will be the major chain initiators in the present instance as even in 1 molar bromal solution the relative absorptions of cobalt-60 gamma rays by bromal and water are in the ratio 1:4.

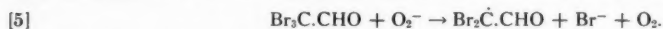
In the absence of oxygen, the hydrogen atoms may react,



though in the present experiments, carried out in the presence of dissolved oxygen, the hydrogen atoms would most likely react with oxygen to form hydroperoxyl radicals, HO_2 . It was found that the yield of acid obtained on irradiating aqueous bromal solutions was increased in the presence of oxygen, so that it would appear that hydroperoxyl radicals are good chain initiators for this reaction. The yield of acid from solutions containing oxygen was decreased by lowering the pH of the solution (Table III), suggesting that the hydroperoxyl radical dissociates,



and that the ion O_2^- is even more reactive in this instance than HO_2 ,

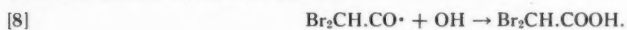


It is known that the ion O_2^- can reduce ions such as Fe^{3+} and Cu^{2+} (1). Reaction [5] might be followed by [6] and [7] to give a chain reaction:



The same chain reaction could be initiated by the hydroxyl radicals formed by irradiation. This suggestion received experimental support from the fact that Fenton's reagent, which produces hydroxyl radicals, will, in fact, initiate a chain reaction in bromal solutions similar to that induced by irradiation. Neither bromine nor any other oxidizing materials were detected in bromal solutions following irradiation, and hypobromous acid, if formed as postulated above, must subsequently be reduced to hydrobromic acid. The reduction might result from reaction between the hypobromous acid and another oxygen-containing species with the liberation of molecular oxygen. Such a reaction occurs between hypobromous acid and hydrogen peroxide.

The formation of dibromoacetic acid by irradiation may be explained by rearrangement of the postulated chain-propagating radical $\text{Br}_2\dot{\text{C}}\cdot\text{CHO}$ to $\text{Br}_2\text{CH}\cdot\text{CO}\cdot$ and subsequent reaction with a hydroxyl radical,



Alternatively, the dibromoacetic acid may be formed from dibromoacetaldehyde, present as an end product of the chain reaction, by consecutive reaction with two hydroxyl radicals:



followed by [8]. However, this seems less likely than the former route as no dibromoacetic acid was isolated from the products formed with Fenton's reagent, though during the final stages the reaction mixture contained relatively large amounts of both dibromoacetaldehyde and hydroxyl radicals.

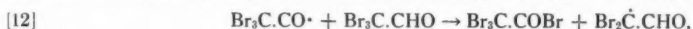
In addition to dibromoacetaldehyde and hydrobromic acid, Fenton's reagent gave tribromoacetic acid, amounting to about 20% of the total material recovered. The proportion of organic acid to dibromoacetaldehyde is thus much greater when Fenton's reagent is used than when the products are formed by radiolysis. In both cases the products are believed to be formed by free-radical mechanisms, though an important difference between the two systems is the concentration of free radicals present during the experiments. During irradiation the concentration of radicals would be very low (the irradiations from which the products were identified lasted several weeks), but the Fenton reactions produced a much greater quantity of radicals and were complete within a few hours. Thus Fenton's reagent would be expected to give products formed by combination of some of the chain-propagating radicals with the large excess of hydroxyl radicals present, such reactions being of little importance in the radiolysis experiments where the radicals formed would be greatly outnumbered by solvent and bromal molecules. The occurrence of a chain-terminating reaction of this nature during the Fenton reaction is supported by the increase in the chain length (Fig. 4) as the concentration of reagent is reduced. The initiation reaction in this case would seem to be



and the chain-terminating reaction with hydroxyl radicals,



The chain reaction, to give dibromoacetaldehyde, might be propagated by



accompanied by hydrolysis of the intermediate acid bromide,



However, the over-all reaction



would give one molecule of tribromoacetic acid for each equivalent of hydrobromic acid formed. This is a much greater proportion of organic acid than has been found with Fenton's reagent, and it is improbable that more than part of the hydrobromic acid and dibromoacetaldehyde could be formed in this manner. Reactions [6] and [7], postulated for the radiation-induced chain reaction, would also be possible and would give the required products without the formation of tribromoacetic acid.

The dependence of the acid yield on the square root of the dose rate (Fig. 3) indicates that the chain-terminating step of the radiolysis reaction is mutual interaction of two of the free radicals taking part in the chain mechanism.

The fate of oxygen present in solution during the radiation-induced reaction, or formed as a consequence of the postulated chain reaction, is not yet established. It does not appear as any simple oxidizing or acidic materials and yet must be used up if the suggested explanation of Fig. 1 is correct. It is possible that the reactions outlined above are accompanied by other reactions involving fission of the carbon-carbon bond of bromal and oxidation of the products.

Work in progress upon related halogen compounds may eventually help to provide a more definite interpretation of the results presented here. It is hoped that the work as a whole will throw light on the reactivity and stability of halogenated free radicals.

ACKNOWLEDGMENT

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THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTRA

III. PYRIDINE AND DEUTERATED PYRIDINES¹

W. G. SCHNEIDER, H. J. BERNSTEIN, AND J. A. POPLE²

ABSTRACT

The proton resonance spectra of pyridine, 2,6-pyridine-*d*₂, 3-pyridine-*d*₁, and 4-pyridine-*d*₁ have been obtained for the pure liquids under conditions of high resolution. The spectra have been analyzed as proton groupings of AB_2X_2 , AB_2 , perturbed ABX , and B_2X_2 respectively. The spin-coupling constants obtained from analysis of the simpler spectra of the deuterated molecules were used to suggest trial solutions for the analysis of the complicated AB_2X_2 spectrum of pyridine. A final set of chemical shifts and spin-coupling constants derived for pyridine give satisfactory agreement between the observed and calculated spectrum.

1. INTRODUCTION

The first two papers of this series dealt with the analysis of nuclear resonance spectra due to certain groupings of two, three, and four nuclei of the same species (with spin $\frac{1}{2}$) where the chemical shift parameters are of the same order of magnitude as the spin-coupling constants. The present paper is concerned with a detailed study of the complex spectrum arising from the five protons in pyridine. Since spin couplings with the nitrogen nucleus are eliminated by quadrupole relaxation, the spectrum may be regarded as a prototype for monosubstituted benzenes. It is found that the signals from the two α -protons are well separated from the β - and γ -protons (Fig. 5), but that the latter overlap in a complex pattern in which about 25 lines have been resolved (Fig. 6). In the notation introduced in Part I (1), therefore, the protons in pyridine would be described as AB_2X_2 , meaning that there are three nuclei (AB_2) (two of which are equivalent) with small relative chemical shift, coupled to two other equivalent nuclei (X_2) whose signals are well separated. The A , B , and X nuclei are identified with the γ -, β -, and α -protons respectively, as shown in Fig. 1.

Since the spectrum of pyridine itself is rather too complicated for an unaided direct analysis, the proton spectra of some partially deuterated pyridines have also been measured and are used as a guide and check on the work. The advantage of using deuterated compounds, of course, is that the electronic structure is unaltered so that the screening and spin-coupling constants for the remaining protons are the same as in the parent compound.

2. GENERAL PROCEDURE

The proton resonance spectrum of pyridine is determined by two relative chemical shifts and six independent spin-coupling constants. The notation used for the latter is illustrated in Fig. 1. As is well known, it is not usually possible to determine all spin-coupling constants uniquely from a spectrum as there are usually indeterminacies in sign. For protons, however, there are theoretical grounds for believing them to be normally positive (3) so we shall assume this throughout.

The procedure adopted is to begin by examining the rather simpler proton spectra of 2,6-pyridine-*d*₂, 4-pyridine-*d*₁, and 3-pyridine-*d*₁. These are all related to types of spectra

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which have been discussed in Parts I and II (4) and they can be used to obtain preliminary estimates of the various constants involved. These values are then used for a full calculation of the spectrum of pyridine itself. Although detailed agreement with observation at this stage is limited, there is sufficient similarity for an assignment of the lines to be carried out. Following this, the values of the parameters are adjusted until the best over-all fit is obtained.

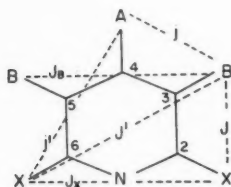


FIG. 1.

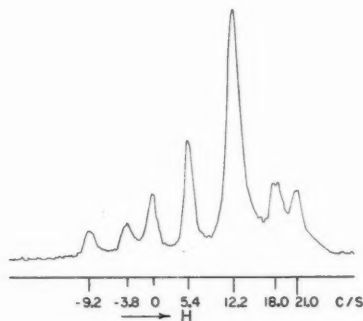
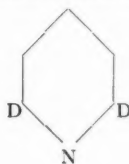


FIG. 2.

3. 2,6-PYRIDINE- d_2 

The proton spectrum* of 2,6-pyridine- d_2 is shown in Fig. 2. As expected it is a typical spectrum of the type AB_2 described in detail in Part I. Analysis leads directly to the values

$$\eta H_0(\sigma_A - \sigma_B) = 14.9 \text{ c./second,}$$

[3.1]

$$j = 7.7 \text{ c./second.}$$

TABLE I

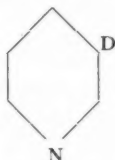
CALCULATED AND OBSERVED SPECTRUM FOR 2,6-PYRIDINE- d_2

A-Lines		B-Lines	
Calc.	Obs.	Calc.	Obs.
-9.2	-9.2	11.8)	12.2
-3.8	-3.8	12.5)	
0	0	18.0	18.0
5.5	5.4	21.0	21.0

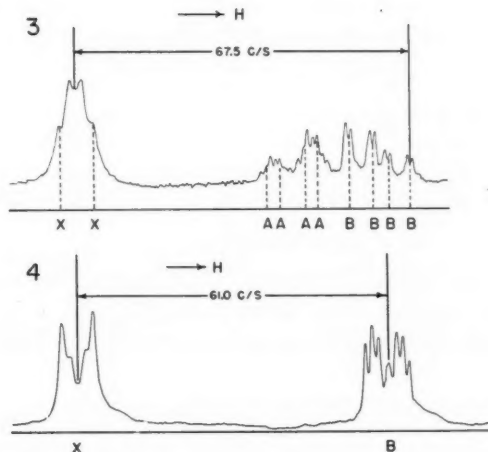
*The spectra described in the present work were measured with a field stabilized Varian High Resolution Spectrometer operating at a fixed frequency of 40 Mc./second. Signal separations were measured by the side-band technique in the usual manner. The samples were measured as pure liquids in a spinning sample tube of 5 mm. O.D. We are indebted to Dr. L. C. Leitch for synthesizing the deuterated pyridines. The sample of pyridine used was reagent grade recovered from the HgCl_2 complex and distilled. Further samples of reagent grade material, which had been distilled in a good fractionating column, were also used and were found to give identical spectra.

A comparison of the observed lines with those calculated using these parameters is given in Table I (measurements relative to the undisplaced *A*-line third from left in Fig. 2).

4. 3-PYRIDINE-*d*₁



The spectrum of 3-pyridine-*d*₁ is shown in Fig. 3. The broad features can be interpreted if we think of it as a modification of the type of spectrum that would be obtained from 2,3-pyridine-*d*₂. (A sample of the latter was not available for examination.) This would have three non-equivalent protons, one well separated from the other two. Such a grouping is described as *ABX* and its analysis was treated in detail in Part I and illustrated by the closely related compound 2,3-lutidine. The spectrum of 3-pyridine-*d*₁ will be of this type with an additional signal from the *X*-proton in the 2-position, which will be expected to interact only weakly with those in positions 4, 5, and 6. The presumed spectrum of 2,3-pyridine-*d*₂ is indicated by dotted vertical lines in Fig. 3. The inner part of the *X*-signal (α -protons) is assigned to the 2-position and so would not appear in 2,3-pyridine-*d*₂. The doubling of the four *B*-signals is attributed to the spin-coupling with the 2-proton. The signals for the *A*-proton (position 4) are apparently complicated by splitting due to the neighboring deuterium nucleus, and only their centers can be measured reliably. This, however, is sufficient for the *ABX* analysis.



FIGS. 3 and 4.

From the presumed spectrum of 2,3-pyridine-*d*₂ we deduce by the method outlined in Part I

$$\begin{aligned}
 \eta H_0(\sigma_A - \sigma_B) &= 15.6 \text{ c./second,} \\
 \eta H_0(\sigma_X - \sigma_A) &= 44.6 \text{ c./second,} \\
 j &= 7.85 \text{ c./second,} \\
 J &= 5.2 \text{ c./second,} \\
 j' &= 1.4 \text{ c./second.}
 \end{aligned}$$

[4.1]

It should be noted that the alternative assignment discussed in Part I is rejected, as it leads to a negative value for j' .

The two constants $\eta H_0(\sigma_A - \sigma_B)$ and j compare reasonably with those obtained from 2,6-pyridine- d_2 . The earlier values should be more reliable, however, as they have been obtained more directly. The value for j' is rather uncertain and it depends crucially on the measured separation of the two shoulders of the X -signal. A considerably more accurate value for this constant is obtained later from pyridine itself.

From the doubling of the B -signals by the 2-proton we estimate, again very roughly,

$$J' = 1.0 \text{ c./second.}$$

[4.2]

5. 4-PYRIDINE- d_1



The spectrum of this compound is shown in Fig. 4. It should be of the type B_2X_2 , the analysis of which has been treated by McConnell, McLean, and Reilly (2). However, the signal from the 3- and 5-protons is complicated by deuterium splitting.

From the separation between the band centers we obtain

$$\eta H_0(\sigma_X - \sigma_B) = 61 \text{ c./second,}$$

[5.1]

in good agreement with the figures obtained from 3-pyridine- d_1 . Some information about the two remaining constants J_B and J_X may be obtained from the X -signal. If we assume that $J_B = J_X$ then the X -signal should consist of a pair of lines separated by $(J+J')$ and an innermost pair separated by

$$\{(J_B + J_X)^2 + (J - J')^2\}^{\frac{1}{2}} - (J_B + J_X).$$

There will also be an outer pair whose intensity is low so that it is unlikely to be observed. The separation of the main pair (6.1 c./second) agrees well with the value of $J+J'$ derived from 3-pyridine- d_1 . To get the correct separation between the inner shoulders we require

$$J_B = J_X = 0.9 \text{ c./second.}$$

[5.2]

These estimates are again very rough and are later modified in connection with the spectrum of pyridine itself.

6. PYRIDINE

The complete spectrum of pyridine itself is illustrated in Fig. 5. The AB part (from protons 3, 4, and 5) under conditions of higher resolution is shown in Fig. 6.

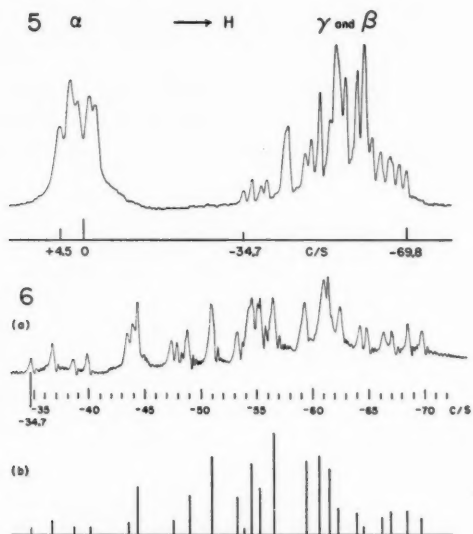
To analyze this spectrum in detail we need to set up the complete quantum mechanical

treatment of a grouping AB_2X_2 on the lines described in Parts I and II. We start with a complete set of basic functions which are most conveniently chosen to be symmetrical or antisymmetrical with respect to reflection in the plane of symmetry. The set chosen is listed in the second column of Table II. The symbols s and a are used for symmetric and antisymmetric functions, and the suffix indicates the total spin component in the direction of the applied field. The diagonal matrix elements of the spin Hamiltonian with respect to

TABLE II
BASIC FUNCTIONS AND DIAGONAL MATRIX ELEMENTS OF HAMILTONIAN FOR AB_2X_2

	Function*		Diagonal matrix element									
	A	BX	ηH_0	$\eta H_{\alpha\beta A}$	$\eta H_{\alpha\beta B}$	$\eta H_{\alpha\beta X}$	J	J'	j	j'	J _B	J _X
$5s_{1/2}$	α	$\alpha\alpha\alpha\alpha$	5/2	-1/2	-1	-1	+1/2	+1/2	+1/2	+1/2	+1/4	+1/4
$1s_{3/2}$	α	$2^{-1/2}\alpha\alpha(\alpha\beta+\beta\alpha)$	3/2	-1/2	-1				+1/2		+1/4	+1/4
$2s_{3/2}$	α	$2^{-1/2}(\alpha\beta+\beta\alpha)\alpha\alpha$	3/2	-1/2		-1				+1/2	+1/4	+1/4
$3s_{3/2}$	β	$\alpha\alpha\alpha\alpha$	3/2	+1/2	-1	-1	+1/2	+1/2	-1/2	-1/2	+1/4	+1/4
$1s_{1/2}$	α	$\alpha\alpha\beta\beta$	1/2	-1/2	-1	+1	-1/2	-1/2	+1/2	-1/2	+1/4	+1/4
$2s_{1/2}$	α	$2^{-1/2}(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha)$	1/2	-1/2			+1/2	-1/2			-1/4	-1/4
$3s_{1/2}$	α	$2^{-1/2}(\alpha\beta\beta\alpha+\beta\alpha\alpha\beta)$	1/2	-1/2			-1/2	+1/2			-1/4	-1/4
$4s_{1/2}$	β	$2^{-1/2}\alpha\alpha(\alpha\beta+\beta\alpha)$	1/2	+1/2	-1				-1/2		+1/4	+1/4
$5s_{1/2}$	α	$\beta\beta\alpha\alpha$	1/2	-1/2	+1	-1	-1/2	-1/2	-1/2	+1/2	+1/4	+1/4
$6s_{1/2}$	β	$2^{-1/2}(\alpha\beta+\beta\alpha)\alpha\alpha$	1/2	+1/2		-1				-1/2	+1/4	+1/4
$1s_{-1/2}$	α	$2^{-1/2}(\alpha\beta+\beta\alpha)\beta\beta$	-1/2	-1/2		+1			-1/2	-1/2	+1/4	+1/4
$2s_{-1/2}$	β	$\alpha\alpha\beta\beta$	-1/2	+1/2	-1	+1	-1/2	-1/2	-1/2	+1/2	+1/4	+1/4
$3s_{-1/2}$	α	$2^{-1/2}\beta\beta(\alpha\beta+\beta\alpha)$	-1/2	-1/2	+1				-1/2		+1/4	+1/4
$4s_{-1/2}$	β	$2^{-1/2}(\alpha\beta\beta\alpha+\beta\alpha\alpha\beta)$	-1/2	+1/2			-1/2	+1/2			-1/4	-1/4
$5s_{-1/2}$	β	$2^{-1/2}(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha)$	-1/2	+1/2			+1/2	-1/2			-1/4	-1/4
$6s_{-1/2}$	β	$\beta\beta\alpha\alpha$	-1/2	+1/2	+1	-1	-1/2	-1/2	+1/2	-1/2	+1/4	+1/4
$1s_{-3/2}$	α	$\beta\beta\beta\beta$	-3/2	-1/2	+1	+1	+1/2	+1/2	-1/2	-1/2	+1/4	+1/4
$2s_{-3/2}$	β	$2^{-1/2}(\alpha\beta+\beta\alpha)\beta\beta$	-3/2	+1/2		+1				+1/2	+1/4	+1/4
$3s_{-3/2}$	β	$2^{-1/2}\beta\beta(\alpha\beta+\beta\alpha)$	-3/2	+1/2	+1				+1/2		+1/4	+1/4
$5s_{-5/2}$	β	$\beta\beta\beta\beta$	-5/2	+1/2	+1	+1	+1/2	+1/2	+1/2	+1/2	+1/4	+1/4
$1a_{3/2}$	α	$2^{-1/2}\alpha\alpha(\alpha\beta-\beta\alpha)$	3/2	-1/2	-1				+1/2		+1/4	-3/4
$2a_{3/2}$	α	$2^{-1/2}(\alpha\beta-\beta\alpha)\alpha\alpha$	3/2	-1/2		-1				+1/2	-3/4	+1/4
$1a_{1/2}$	α	$2^{-1/2}(\alpha\beta\alpha\beta-\beta\alpha\beta\alpha)$	1/2	-1/2			+1/2	-1/2			-1/4	-1/4
$2a_{1/2}$	α	$2^{-1/2}(\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)$	1/2	-1/2			-1/2	+1/2			-1/4	-1/4
$3a_{1/2}$	β	$2^{-1/2}\alpha\alpha(\alpha\beta-\beta\alpha)$	1/2	+1/2	-1				-1/2		+1/4	-3/4
$4a_{1/2}$	β	$2^{-1/2}(\alpha\beta-\beta\alpha)\alpha\alpha$	1/2	+1/2		-1				-1/2	-3/4	+1/4
$1a_{-1/2}$	α	$2^{-1/2}(\alpha\beta-\beta\alpha)\beta\beta$	-1/2	-1/2		+1				-1/2	-3/4	+1/4
$2a_{-1/2}$	α	$2^{-1/2}\beta\beta(\alpha\beta-\beta\alpha)$	-1/2	-1/2	+1				-1/2		+1/4	-3/4
$3a_{-1/2}$	β	$2^{-1/2}(\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)$	-1/2	+1/2			-1/2	+1/2			-1/4	-1/4
$4a_{-1/2}$	β	$2^{-1/2}(\alpha\beta\alpha\beta-\beta\alpha\beta\alpha)$	-1/2	+1/2			+1/2	-1/2			-1/4	-1/4
$1a_{-3/2}$	β	$2^{-1/2}(\alpha\beta-\beta\alpha)\beta\beta$	-3/2	+1/2		+1				+1/2	-3/4	+1/4
$2a_{-3/2}$	β	$2^{-1/2}\beta\beta(\alpha\beta-\beta\alpha)$	-3/2	+1/2	+1				+1/2		+1/4	-3/4

*The ordering of the nuclei is 4, 5, 2, 6 (see Fig. 1). Thus $\alpha\beta\beta\alpha\alpha$ is short for $\alpha(4) \beta(5) \beta(2) \alpha(6) \alpha(6)$.



FIGS. 5 and 6.

these functions are also listed in Table II, being evaluated according to the rules summarized in Part I. There are no off-diagonal matrix elements between functions of different symmetry or between functions of different total spin. This divides the total matrix into submatrices as indicated by the solid horizontal lines. Further simplification follows if we neglect off-diagonal matrix elements between functions whose diagonal elements differ by an amount involving the large chemical shift between the X and A, B nuclei. This is the simplification which follows when we proceed from AB_2C_2 to AB_2X_2 . Further subdivision of the matrix is indicated by dotted lines, the largest order of secular equation to be solved now being three. Off-diagonal matrix elements in these submatrices are listed in Table III.

TABLE III
OFF-DIAGONAL MATRIX ELEMENTS OF HAMILTONIAN FOR AB_2X_2

$(2s_{3/2} \mathcal{H} 3s_{3/2})$	$j/\sqrt{2}$	$(1a_{1/2} \mathcal{H} 2a_{1/2})$	$\frac{1}{2}(J_X - J_B)$
$(2s_{1/2} \mathcal{H} 3s_{1/2})$	$\frac{1}{2}(J_B + J_X)$	$(1a_{1/2} \mathcal{H} 3a_{1/2})$	$\frac{1}{2}j$
$(2s_{1/2} \mathcal{H} 4s_{1/2})$	$\frac{1}{2}j$	$(2a_{1/2} \mathcal{H} 3a_{1/2})$	$-\frac{1}{2}j$
$(3s_{1/2} \mathcal{H} 4s_{1/2})$	$\frac{1}{2}j$	$(2a_{-1/2} \mathcal{H} 3a_{-1/2})$	$-\frac{1}{2}j$
$(5s_{1/2} \mathcal{H} 6s_{1/2})$	$j/\sqrt{2}$	$(2a_{-1/2} \mathcal{H} 4a_{-1/2})$	$\frac{1}{2}j$
$(1s_{-1/2} \mathcal{H} 2s_{-1/2})$	$j/\sqrt{2}$	$(3a_{-1/2} \mathcal{H} 4a_{-1/2})$	$\frac{1}{2}(J_X - J_B)$
$(3s_{-1/2} \mathcal{H} 4s_{-1/2})$	$\frac{1}{2}j$		
$(3s_{-1/2} \mathcal{H} 5s_{-1/2})$	$\frac{1}{2}j$		
$(4s_{-1/2} \mathcal{H} 5s_{-1/2})$	$\frac{1}{2}(J_B + J_X)$		
$(1s_{-3/2} \mathcal{H} 2s_{-3/2})$	$j/\sqrt{2}$		

For any given set of values of the screening and spin-coupling constants we can now obtain the complete set of energy levels as the eigenvalues of these matrices. The station-

ary state wave functions are linear combinations of the basic functions given by the corresponding eigenvectors. It is convenient to catalogue the energy levels in the same way as the basic functions. Thus the function $2s_{1/2}'$, for example, becomes the stationary state wave function $2s_{1/2}$ as the off-diagonal matrix elements are allowed to tend continuously to zero.

Transitions only occur between states of the same symmetry with total spin differing by ± 1 . For AB_2X_2 there are 110 in all. These may be classified into 20 *A*-transitions, 24 *B*-transitions, 24 *X*-transitions, and 42 combination transitions by examining the corresponding basic functions. (A transition is said to be of the combination type if the corresponding basic functions differ in the spins of more than one nucleus.) Combination transitions will be weak and we shall not include them in the analysis.

After several trial calculations, the following were selected as optimum values of the

TABLE IV

Transition	Calc. energy	Observed energy	Calc. intensity
A-Lines			
$3s_{3/2} \rightarrow s_{5/2}$	-34.7	-34.7	0.4
$4s_{1/2} \rightarrow 1s_{3/2}$	-36.6	-36.6	0.4
$3a_{1/2} \rightarrow 1a_{3/2}$	-36.7		
$2s_{-1/2} \rightarrow 1s_{1/2}$	-38.7	-38.5	0.4
$4s_{-1/2} \rightarrow 2s_{1/2}$	-38.9	—	0.1
$3a_{-1/2} \rightarrow 1a_{1/2}$	-39.0	—	0.0
$6s_{1/2} \rightarrow 2s_{3/2}$	-39.9	-39.7	0.5
$5s_{-1/2} \rightarrow 2s_{1/2}$	-43.1	-43.9	0.4
$4a_{-1/2} \rightarrow 1a_{1/2}$	-43.4		0.5
$4a_{1/2} \rightarrow 2a_{3/2}$	-43.7		1.0
$3a_{-1/2} \rightarrow 2a_{1/2}$	-44.2		0.4
$2s_{-3/2} \rightarrow 1s_{-1/2}$	-44.3	-47.3	0.6
$4s_{-1/2} \rightarrow 3s_{1/2}$	-44.5		0.8
$1a_{-3/2} \rightarrow 1a_{-1/2}$	-47.5		1.0
$4a_{-1/2} \rightarrow 2a_{1/2}$	-48.6	—	0.2
$5s_{-1/2} \rightarrow 3s_{1/2}$	-48.7	—	0.1
$6s_{-1/2} \rightarrow 5s_{1/2}$	-48.9	-48.8	2.2
$2a_{-3/2} \rightarrow 2a_{-1/2}$	-50.9	-51.0	2.1
$3s_{-3/2} \rightarrow 3s_{-1/2}$	-51.0		2.1
$s_{-5/2} \rightarrow 1s_{-3/2}$	-53.1	-52.8	2.0
B-Lines			
$3s_{1/2} \rightarrow 1s_{3/2}$	-53.7	-54.5	0.5
$2a_{1/2} \rightarrow 1a_{3/2}$	-54.4		0.7
$5s_{1/2} \rightarrow 2s_{3/2}$	-54.5		3.2
$2s_{3/2} \rightarrow s_{5/2}$	-55.1	-55.1	2.7
$2a_{-1/2} \rightarrow 1a_{1/2}$	-56.3	-56.5	2.4
$3s_{-1/2} \rightarrow 2s_{1/2}$	-56.5		3.2
$2s_{1/2} \rightarrow 1s_{3/2}$	-59.3	-59.3	2.1
$1a_{1/2} \rightarrow 1a_{3/2}$	-59.6		2.0
$6s_{1/2} \rightarrow 3s_{3/2}$	-60.3		1.3
$1s_{-3/2} \rightarrow 1s_{-1/2}$	-60.7	-61.0, -62.4	3.0
$1s_{-1/2} \rightarrow 1s_{1/2}$	-61.3		2.6
$2a_{-1/2} \rightarrow 2a_{1/2}$	-61.5		0.6
$4s_{-1/2} \rightarrow 4s_{1/2}$	-61.6		0.8
$3a_{-1/2} \rightarrow 3a_{1/2}$	-61.9	-64.2	0.8
$3s_{-1/2} \rightarrow 3s_{1/2}$	-62.1		0.7
$6s_{-1/2} \rightarrow 6s_{1/2}$	-63.5		0.8
$2a_{-3/2} \rightarrow 4a_{-1/2}$	-63.8		0.3
$3s_{-3/2} \rightarrow 5s_{-1/2}$	-64.4	-64.8	0.4
$5s_{-1/2} \rightarrow 4s_{1/2}$	-65.8	-66.4	0.3
$4a_{-1/2} \rightarrow 3a_{1/2}$	-66.3		0.6
$2s_{-3/2} \rightarrow 2s_{-1/2}$	-66.9	-67.2	1.4
$2a_{-3/2} \rightarrow 3a_{-1/2}$	-68.2	-68.5	0.6
$3s_{-3/2} \rightarrow 4s_{-1/2}$	-68.6		0.5
$s_{-5/2} \rightarrow 2s_{-3/2}$	-69.5	-69.8	1.0

TABLE IV (concluded)

Transition	Calc. energy	Observed energy	Calc. intensity
X-Lines			
$3s_{1/2} \rightarrow 2s_{3/2}$	+5.5	+4.5	0.4
$1a_{-1/2} \rightarrow 1a_{1/2}$	+4.9		0.5
$1s_{1/2} \rightarrow 1s_{3/2}$	+4.2		2.0
$1s_{3/2} \rightarrow 5s_{3/2}$	+4.1		2.0
$4s_{1/2} \rightarrow 3s_{3/2}$	+2.2		2.0
$2a_{1/2} \rightarrow 2a_{3/2}$	+2.2	+2.5	1.5
$2s_{-1/2} \rightarrow 4s_{1/2}$	+2.1		2.0
$1s_{-1/2} \rightarrow 2s_{1/2}$	+1.8		1.6
$3a_{-1/2} \rightarrow 4a_{1/2}$	+1.7		0.8
$2s_{-3/2} \rightarrow 5s_{-1/2}$	+1.0		1.0
$4s_{-1/2} \rightarrow 6s_{1/2}$	+0.9	+0.9	1.0
$1a_{-3/2} \rightarrow 4a_{-1/2}$	+0.8		1.2
$2s_{1/2} \rightarrow 2s_{3/2}$	+0.1		1.6
$1a_{-1/2} \rightarrow 2a_{1/2}$	-0.3		1.5
$1s_{-3/2} \rightarrow 3s_{-1/2}$	-2.0		2.0
$3s_{-1/2} \rightarrow 5s_{1/2}$	-2.1	-1.2	2.0
$4a_{-1/2} \rightarrow 4a_{1/2}$	-2.7		1.2
$1a_{1/2} \rightarrow 2a_{3/2}$	-3.0		0.5
$2s_{-3/2} \rightarrow 4s_{-1/2}$	-3.2		1.0
$5s_{-1/2} \rightarrow 6s_{1/2}$	-3.3		1.0
$1s_{-1/2} \rightarrow 3s_{1/2}$	-3.4	-2.9	0.4
$1a_{-3/2} \rightarrow 3a_{-1/2}$	-3.6		0.8
$s_{-5/2} \rightarrow 3s_{-3/2}$	-4.1		2.0
$3s_{-3/2} \rightarrow 6s_{-1/2}$	-4.2		2.0

chemical shifts and spin-coupling constants:*

$$\begin{aligned}
 \eta H_0(\sigma_A - \sigma_B) &= 15.0 \text{ c./second}, j = 7.5 \text{ c./second}, \\
 \eta H_0(\sigma_X - \sigma_A) &= 45.6 \text{ c./second}, j' = 1.9 \text{ c./second}, \\
 J &= 5.5 \text{ c./second}, \\
 J' &= 0.9 \text{ c./second}, \\
 J_B &= 1.6 \text{ c./second}, \\
 J_X &= 0.4 \text{ c./second}.
 \end{aligned}$$

The calculated energies and intensities of all the transitions (other than combination lines) are listed in Table IV together with the observed positions. Both sets of figures are measured relative to the center of the band arising from α -protons (see Fig. 5). The detailed agreement with experiment for the β - γ region is illustrated in Fig. 6(b). For purposes of illustration, some lines predicted to be closer than ~ 0.5 c./second have been coalesced in this figure.

The above analysis is valid for the spectrum of pure liquid pyridine. The effect of solvent dilution on the chemical shifts of the AB - and X -protons in pyridine was also investigated. From the spectrum of 3,5-pyridine- d_2 as a function of concentration in CCl_4 , the chemical shift at infinite dilution is found to be $\eta H_0(\sigma_X - \sigma_A) = 37$ c./second, to be compared with the value of 45.6 c./second for liquid pyridine. From the spectrum of 4-pyridine- d_1 at infinite dilution the chemical shift difference $\eta H_0(\sigma_X - \sigma_B)$ is found to be 54 c./second. This is to be compared with the value of 60.6 c./second found for liquid pyridine. The difference $\eta H_0(\sigma_A - \sigma_B)$ at infinite dilution is the same as for the liquid within the experimental error. Since the X - A and X - B chemical shifts vary with dilution it is to

*These values are considerably more accurate than chemical shift values previously reported by E. B. Baker (J. Chem. Phys. **23**, 1981 (1955)) and H. J. Bernstein and W. G. Schneider (J. Chem. Phys. **24**, 469 (1956)). The values in the latter reference were derived from a lower resolution spectrum permitting only partial analysis which led to an incorrect assignment of the fine structure components for the β - and γ -protons of pyridine.

be expected that the appearance of the pyridine spectrum will be somewhat modified. It is interesting to note that the origin of the *X*-proton signal changes relative to the *A*- and *B*-signals upon dilution.

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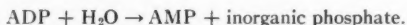
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THE NON-ENZYMATIC HYDROLYSIS OF ADENOSINE DIPHOSPHATE¹

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ABSTRACT

The kinetics of the non-enzymatic hydrolysis of adenosine diphosphate in aqueous solution have been studied at pH 3.5 to 10.5 and temperatures from 80° to 95° C. The reaction has been followed by measuring colorimetrically the inorganic phosphate liberated according to the over-all reaction



The reaction has been found to be first order with respect to ADP concentration and to be catalyzed by hydrogen ions. From rate studies at pH 8.0 an activation energy of 24.2 kcal./mole was derived. A mechanism is proposed to account for the observed facts and the mechanism for the hydrolysis of adenosine triphosphate is also discussed.

INTRODUCTION

The observations that adenosine triphosphate (ATP) (24) and to a lesser extent adenosine diphosphate (ADP) (3) cause myosin threads to contract have led to theories of muscle action (21) in which these compounds play an important role by virtue of their "high-energy phosphate bonds". This last nomenclature refers to the relatively high free energy decreases associated with the hydrolyses of these compounds compared to adenylic acid (AMP). Kalckar (13) has suggested that this difference is due to relative resonance stabilization of the reaction product and Hill and Morales (12) have shown that electrostatic repulsion between the terminal phosphate groups may be an additional factor.

Various values for the standard free energy change (ΔF°) for the hydrolysis of ATP,



have been reported (18, 21, 17, 20) although it is not always clear to what thermodynamic standard state these refer. The latest value $\Delta F^\circ = -7.8$ kcal./mole due to Robbins and Boyer (23) has been calculated at pH 7.0 and 30° C. and adopts the convention that the activity of water is 55.5 moles/liter.

From the recent data of Bowen and Kerwin (4) for the myokinase system



it is possible to make a rough estimate of ΔF° for this equilibrium under identical conditions as $\sim +0.5$ kcal./mole. Coupling these values we obtain as an estimate for the free energy of hydrolysis of ADP at pH 7.0 and 30° a value of ~ -7.3 kcal./mole.

Studies of the kinetics of these hydrolyses have so far been mainly limited to the enzyme-catalyzed hydrolyses of ATP (22, 14). However, some measurements have been made by Friess (10) on the acid-catalyzed hydrolysis of ATP and by Couture and Ouellet for this hydrolysis at pH 8-9 (7).

It seemed therefore of interest to extend this kinetic study to ADP in order to make some comparisons.

The present work has involved a study of the non-enzymatic hydrolysis of adenosine diphosphate over a wide range of pH (3.5 to 10.5) in aqueous solutions at temperatures from 80° to 95° C.

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EXPERIMENTAL RESULTS

Materials

ADP was supplied by the Nutritional Biochemicals Corporation as the monosodium salt and was stated to be chromatographically purified. Analysis indicated an initial inorganic phosphate content of 8–10%. Solutions of about $5.0 \times 10^{-2} M$ were prepared, neutralized to pH 8.0 with sodium hydroxide, and stored in a refrigerator. The concentration of these solutions was measured by their ultraviolet adsorption at 260 m μ in a Beckman model D.U. spectrophotometer, taking the extinction coefficient as 1.47×10^4 based on data for ADP and AMP given by Gulland and Holiday (11).

Buffer solutions were prepared using standard reagents, some according to the methods prescribed by the National Bureau of Standards (2). The presence of phosphate in the usual buffers around pH 7 made their use undesirable, and for this range a "tris" (tris hydroxymethyl amino methane) buffer was used, its heat of ionization being determined to enable the calculation of its pH at any temperature from 80 to 90° C.

Most of the buffer solutions were used at 92.0° C., at which temperature their pH values were measured using Beckman high temperature glass (1190–60) and reference calomel (8970–13) electrodes calibrated by means of Beckman standard buffer solution 3581 (pH 7.10 at 92.0° C.).

Apparatus

Some of the early kinetic runs were carried out in 100 ml. glass-stoppered reaction flasks immersed in an electrically heated oil bath. The temperature of this bath was controlled by a mercury thermoregulator and a relay to $\pm 0.1^\circ C.$ at 80–90° C. However, for experiments in which the rate of reaction was more rapid, it was found necessary to reduce the time of heating of reactants to a minimum and to stir the reaction mixture continuously.

These necessities were provided for in the apparatus shown in Fig. 1. By means of

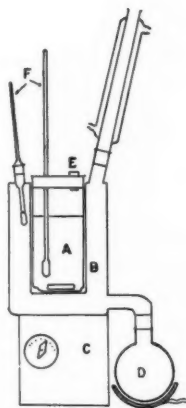


FIG. 1. A—The reaction mixture, B—vapor jacket, C—magnetic stirrer, D—boiler containing benzene/toluene mixture, E—rubber stopper, F—thermometers.

this apparatus the temperature was kept constant by refluxing a benzene/toluene mixture around a beaker containing the reactants. The temperature could be controlled to $\pm 0.1^\circ C.$ and altered by altering the composition of the mixture. The reactants were stirred con-

tinuously by a magnetic stirrer. Buffer solution (80 ml.) containing the requisite amount of KCl to keep the ionic strength constant was placed in the inner beaker and brought to the required temperature, and 1 ml. of concentrated ($\sim 5 \times 10^{-2} M$) ADP solution was then added. Samples of about 2 ml. of reaction mixture were removed at definite time intervals, and reaction was stopped by bringing them rapidly to about 25° C. The fractions were analyzed for inorganic orthophosphate by the colorimetric technique of Lowry and Lopez (19). Inorganic pyrophosphate was analyzed for by the method of Lipmann and co-workers (6) and was found to be absent.

Velocity constants were measured from the slope of "phosphate produced" versus time curves, which were linear for the first 10–20% hydrolysis. The initial ADP concentrations were corrected for the small amount of inorganic phosphate present initially.

Determination of Reaction Order with Respect to ADP

A series of runs was carried out to determine the order of reaction with respect to ADP. These were done by adding various volumes of ADP solution to 30 ml. buffer solution (0.33 *M* sodium hydroxide, 0.66 *M* boric acid, pH = 8.9 at 92.6° C.) and sufficient distilled water to bring the total volume to 100 ml. Solid KCl was added to keep the ionic strength constant at 0.1. The reaction mixtures were heated to 92.6° C. in an oil bath and 1-ml. samples were extracted for analysis at convenient time intervals. The results are expressed in a plot of rate vs. $[\text{ADP}]_0$ in Fig. 2.

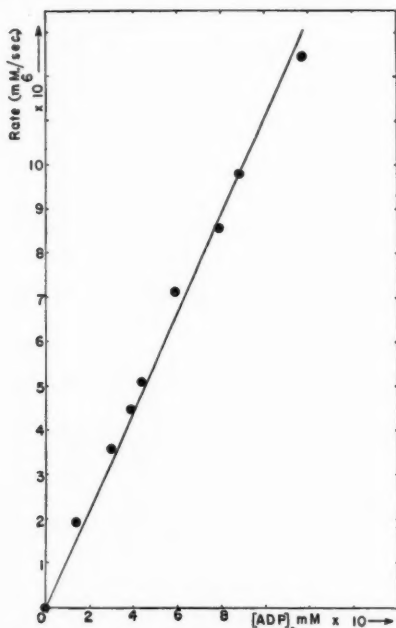


FIG. 2. Temperature 92.6° C., ionic strength 0.1, pH 8.9.

The Effect of Hydrogen Ion

Keeping $[\text{ADP}]_0$ constant at $0.576 \times 10^{-3} M$, runs were carried out using different buffer solutions from pH 3.5 to 10.5 at 92.6° C. These were done using the vapor-jacket apparatus employing 80 ml. buffer solution and 1 ml. ADP solution by the method outlined

above. The kinetic results at high pH values were identical with those obtained using the oil bath. Fig. 3 shows a plot of rate vs. pH at an ionic strength of 0.1 and a temperature of 92.6° C.

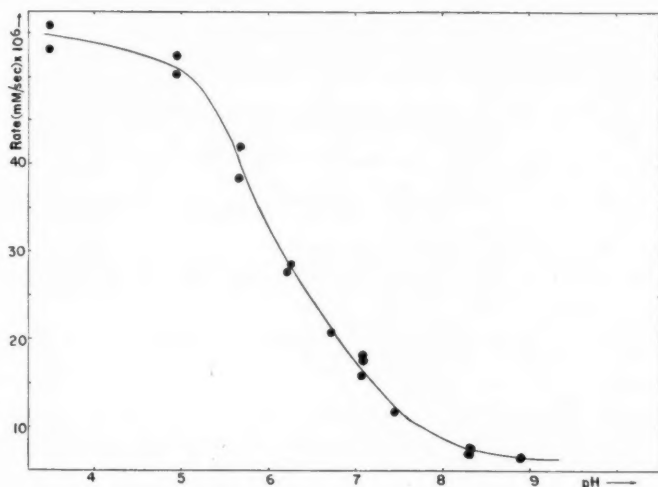


FIG. 3. $[\text{ADP}]_0 = 0.576 \times 10^{-3} M$, ionic strength 0.1, temperature 92.6° C.

The effect of hydrogen ion was investigated at three different temperatures, and Fig. 4 shows plots of rate versus $[\text{H}^+]$ at 92.6°, 87.8°, and 80.0° C. These results were obtained using boric acid and "tris" buffer solutions.

The Activation Energy at pH 8.0

The activation energy at pH 8.0 was calculated by determining the rate of reaction at different temperatures for the same concentration of ADP and a boric acid/sodium hydroxide buffer. The pH of the buffer was adjusted to 8.0 at each temperature by addition of small quantities of solid boric acid. The ionic strength was 0.1 in all experiments. Fig. 5 shows a plot of log rate vs. $1/T^\circ K$. for these experiments from which an activation energy of 24.2 kcal. was derived.

Addition of Pyridine

A few experiments were done in which amounts of pyridine up to $2.23 \times 10^{-3} M$ were added to $0.82 \times 10^{-3} M$ ADP at pH 8.9 and 92.6° C. No effect on the rate of hydrolysis was observed.

DISCUSSION

The hydrolysis of adenosine diphosphate can be seen from Fig. 2 to be first order with respect to ADP concentration at pH 8.9 and 92.6° C., and it was assumed that this is also valid at the other pH values and temperatures at which the hydrolysis was studied.

The over-all hydrolysis may be represented by the equation



No evidence for pyrophosphate was found in the present work in agreement with the

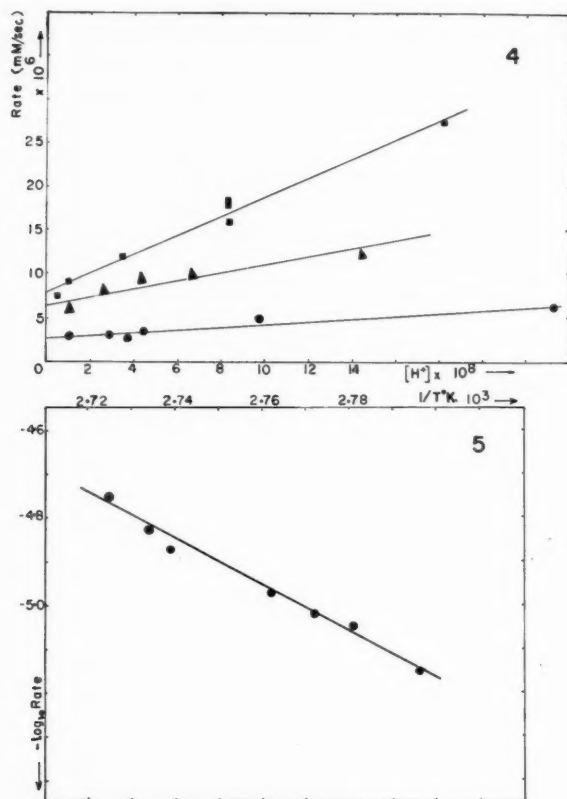


FIG. 4. $[\text{ADP}]_0 = 0.576 \times 10^{-3} M$, ionic strength 0.1. ■, 92.6°C .; ▲, 87.8°C .; ●, 80.0°C .
 FIG. 5. $[\text{ADP}]_0 = 0.576 \times 10^{-3} M$, ionic strength 0.1; pH 8.0.

results of Friess on the analogous hydrolyses of pyrophosphoric acid (8) and fructose-6-phosphoric acid (9).

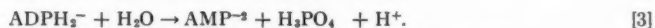
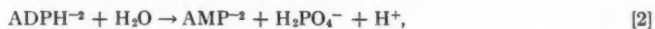
The hydrolysis of ADP shows strong similarities with the hydrolyses of acetyl phosphate (15) and monoalkyl phosphoric acids (5), where similar rate vs. pH curves have been obtained for the pH region 3.5–10.5.

The plots of rate vs. $[\text{H}^+]$ show that at constant $[\text{ADP}]$ and at pH > 6.5 the rate can be expressed by an equation of the type

$$\text{rate} = a + b[\text{H}^+],$$

where a and b are constants. This equation is similar to that for carboxylic esters and phosphoric esters (see (15)) in that it contains a term independent of hydrogen ion, which may be regarded as due to "normal" hydrolysis or attack by a neutral water molecule. Attack by OH^- ions seems unimportant in the range of pH studied, probably owing to the high negative charge surrounding the phosphorus atom. For similar reasons the OH^- attack on acetyl phosphate (15) was considered to take place at the carbonyl carbon atom rather than at the phosphorus atom.

The most reasonable explanation for the ADP hydrolysis appears to involve a nucleophilic attack by a water molecule on the particular ADP species in solution, e.g.,



Assuming that at pH > 6.5, the rate is mainly due to reactions [1] and [2],

$$\text{rate} = \{k_1[\text{ADP}^{-3}] + k_2[\text{ADPH}^{-2}]\} [\text{H}_2\text{O}],$$

and expressing $[\text{ADP}^{-3}]$ and $[\text{ADPH}^{-2}]$ in terms of $[\text{ADP}]_0$ and the equilibrium constant

$$K_a = [\text{ADP}^{-3}][\text{H}^+]/[\text{ADPH}^{-2}],$$

$$\text{rate} = [\text{ADP}]_0[\text{H}_2\text{O}]\{(k_1 + k_2[\text{H}^+]/K_a)/(1 + [\text{H}^+]/K_a)\}.$$

If it is assumed that $[\text{H}^+] < K_a$ (from the data of Alberty *et al.* (1) $\text{p}K_a = 6.68$ at 25° C.), then

$$d[\text{PO}_4^{\equiv}] = [\text{ADP}]_0[\text{H}_2\text{O}]\{k_1 + k_2[\text{H}^+]/K_a\},$$

which is of the form found experimentally. Activation energies corresponding to k_1 and k_2/K_a have been found to be 22.9 ± 3.3 kcal./mole (in reasonable agreement with the value 24.2 kcal./mole obtained from Fig. 5) and 37.5 ± 2.8 kcal./mole. The activation energy for k_2 is therefore likely to be greater than 37.5 kcal. by an amount $R d \log_e K_a / d(1/T)$, which from the data of Alberty *et al.* (1) may be estimated to be ~ 0.5 kcal./mole.

Assuming that at pH > 8.0 the rate can be expressed by

$$\text{rate} = k_1[\text{ADP}]_0[\text{H}_2\text{O}],$$

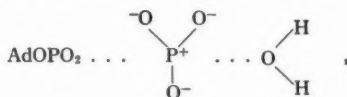
then from the data given in Fig. 2

$$k_1 = 2.07 \times 10^{-7} \text{ l. mole}^{-1} \text{ sec.}^{-1},$$

and taking $E_1 = 24.0$ kcal./mole it can be calculated that the entropy of activation associated with reaction [1] is

$$\Delta S_1^\ddagger = -1.2 \text{ e.u.}$$

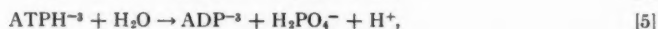
Following Koshland's (16) explanation for the nucleophilic displacement mechanism of enzymatic ATP hydrolysis a reasonable activated complex for reaction [1] would be



although whether this would be a transition complex or a stable intermediate is uncertain.

The lack of evidence for any nucleophilic attack by pyridine on the phosphorus atom is in agreement with the explanation that pyridine catalyzes the hydrolysis of acetyl phosphate by attack at the carbon atom (15).

A similar mechanism may be proposed for the hydrolysis of ATP, i.e.,



and hence,

$$\text{rate} = [\text{ATP}]_0[\text{H}_2\text{O}]\{k_4 + k_5[\text{H}^+]/K_a'\},$$

where

$$K_a' = [\text{ATP}^{-4}][\text{H}^+]/[\text{ATPH}^{-3}].$$

The results of Couture and Ouellet (7) would indicate that k_4 for ATP is much less important than k_5 . These authors deduced a rate constant $k' = \text{rate}/[\text{ATP}][\text{H}^+]$. Hence $k' = k_5[\text{H}_2\text{O}]/K_a'$, neglecting k_4 .

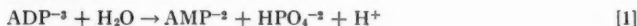
The corresponding entropy changes are related by

$$\Delta S_5^\ddagger = \Delta S^{\ddagger'} + \Delta S_a' - R \ln[55.5]$$

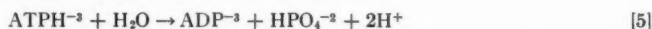
where ΔS_5^\ddagger and $\Delta S^{\ddagger'}$ are entropies of activation associated with k_5 and k' respectively and $\Delta S_a'$ is the entropy change derived from the equilibrium constant K_a' .

An estimate of $\Delta S_a'$ from the data of Alberty *et al.* (1) is given by $\Delta S_a' = -32$ to -34 e.u.

Couture and Ouellet found $\Delta S^{\ddagger'}$ to be $+39.0$ e.u. and hence $\Delta S_5^\ddagger = -33.0 + 39.0 - 8.0 = -2.0 \pm 1.0$ e.u. It is interesting to note that this value agrees well with the value $\Delta S_1^\ddagger = -1.2$ e.u. derived from the work described in this paper. The entropies of activation associated with the reactions



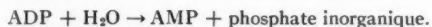
and



are thus similar, as might be expected from the similarity of their charges and structures.

RÉSUMÉ

La cinétique de l'hydrolyse non-enzymatique de l'adénosine diphosphate en solution aqueuse a été étudiée à des pH allant de 3.5 à 10.5 et à des températures allant d'environ 80° à 95° C. La réaction a été suivie par la mesure colorimétrique du phosphate inorganique libéré selon la réaction



La réaction est du premier ordre en ADP et est catalysée par les ions hydrogène. La mesure des taux à pH 8.0 a donné une énergie d'activation de 24.2 kcal./mole. On propose un mécanisme pour tenir compte des faits expérimentaux dans ce cas-ci et dans le cas de l'hydrolyse de l'ATP dans des conditions semblables.

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HYDROGENOLYSIS OF CARBOHYDRATES

III. FURTHER OBSERVATIONS ON THE REDUCTION OF METHYL α -D-GLUCOPYRANOSIDE¹

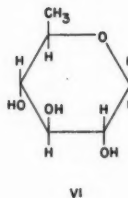
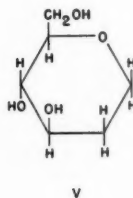
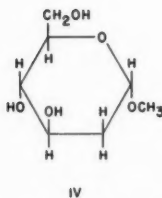
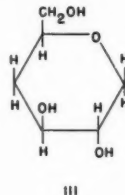
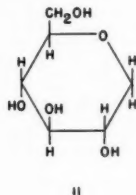
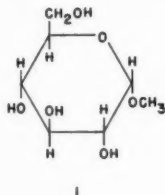
E. VON RUDLOFF AND A. P. TULLOCH²

ABSTRACT

The hydrogenolysis of methyl α -D-glucopyranoside at 180° to 220° C. was found to yield in addition to the polyols obtained at 240° substantial quantities of hydro-D-glucal (2-deoxy-1,5-anhydro-D-sorbitol), smaller amounts of 2-deoxymethyl glucoside, and the hitherto unknown hydro-D-altral, as well as trace amounts of several other unidentified deoxy-glycosides and 1,5-anhydrohexitols. These findings accordingly revise the reduction mechanism proposed earlier and show that inversion of one or more hydroxyl groups can occur during the hydrogenolysis.

In the previous paper of this series (13) it was shown that the hydrogenolysis of methyl α -D-glucopyranoside at 240–250° C. and 250 atmospheres pressure, using copper chromium oxide as catalyst and dioxane as solvent, produced as major reaction products, besides water and methanol, 2-hydroxymethyl-4,5-dihydroxytetrahydropyran (4-deoxy-1,5-anhydrohexitol), isomeric hexanediols, 1,2-propanediol, and ethanediol. The hydrogenolysis of methyl glucoside has now been studied under milder reaction conditions and the results lead to a revision of the reduction mechanism proposed earlier (2).

Previously (2) it was thought that the initial point of attack in the hydrogenolysis of methyl glycosides was at the methoxyl group at C1, and that the resulting 1,5-anhydro-polyol was then further reduced according to Adkins' β -rule (1). With methyl glucoside (I) one would, therefore, have expected reduction to polygalitol (1,5-anhydro-D-sorbitol) (II) and then preferentially to 4-deoxy-1,5-anhydro-D-sorbitol (III), since the hydroxyl



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²National Research Council of Canada Postdoctorate Fellow 1956–57.

at C4 is in β -position to the one at C2 and that at C6; smaller yields of the 2-deoxy (V) and 6-deoxy (VI) isomers would also be expected.

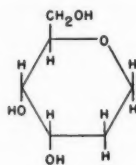
It has now been found that appreciable quantities of 2-deoxymethyl glucoside (IV) and of hydro-D-glucal (V) are formed, showing that reduction may occur at a hydroxyl group before removal of the methoxyl group and also that the reduction need not necessarily proceed according to the β -rule. However, the reaction does not appear to be completely random, since neither a 3-deoxy nor a 6-deoxy compound could be isolated. Although these compounds may be produced in very small quantities it follows that the reduction occurs preferentially at carbons 1, 2, and 4. Also the 4-deoxy isomer (III) is found to be remarkably stable in rehydrogenation, showing that compounds having no hydroxyl groups in the β -position survive the reaction.

The hydrogenolysis of methyl glucoside was greatly influenced by the reaction temperature, especially in the range 180° to 240° C. Under the conditions employed no detectable reaction occurred below 180° C. At 180° C. about 5 to 10%, and at 200° C. more than 60% of the methyl glucoside reacted, and at higher temperatures little or no unreacted starting material was recovered. The reaction product was always a very complex mixture of polyols. At 180° and 200° C. only cyclic polyols were obtained, but at higher temperatures the yield of these cyclic compounds decreased with a corresponding increase in the yield of the open-chain polyols previously reported (13). The yield of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran (III) was 15 to 25% and did not appear to be much influenced by the reaction temperature. A considerable proportion of the reaction product could not be resolved into pure components.

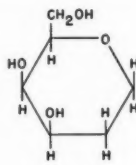
The various polyols and sugars produced were separated mainly by chromatography on cellulose columns (5), using paper chromatography for qualitative purposes. In this manner it was found that in the reaction at 200° to 220° C. hydro-D-glucal (2-deoxy-1,5-anhydro-D-sorbitol) (V) was a major reaction product and that small but significant quantities of 2-deoxymethyl α -D-glucopyranoside and two new tetrahydropyrantriols having melting points 66–69° and 104° C., respectively, are produced.

The latter triol, melting point 104° C., $[\alpha]_D +72.6^\circ$, and R_f 0.52, was isolated in about 1% yield (based on the amount of reacted glucoside). It was found to consume 1 mole of periodate per mole and its infrared spectrum differed from that of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran. The compound took up almost 1 mole of lead tetraacetate per mole about 12 times as fast as did hydro-D-glucal, showing that it contains two hydroxyl groups in the α -cis-position. From the results of these oxidations it follows that the triol must be either a 2-deoxy or a 4-deoxy 1,5-anhydrohexitol. Oxidation with periodate followed by sodium borohydride reduction produced 2-O-(γ -hydroxy-*n*-propyl)-glycerol (X), which was characterized by its *p*-nitrobenzoate. The same product was obtained when hydro-D-glucal (V) was degraded by the same procedure. Also, on periodate oxidation both isomers gave a solution which had the same specific optical rotation, $[\alpha]_D -0.6^\circ$, confirming that the same dialdehyde (IX) was produced in both instances. Thus, the compound must be a 2-deoxy isomer and could be either hydro-D-altral (VII) or hydro-D-galactal (VIII).

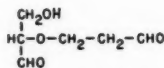
Lohaus and Widmaier (8) report for hydro-D-galactal a melting point of 128° C. and $[\alpha]_D +48.1^\circ$. It, therefore, was concluded that the compound is the previously unknown hydro-D-altral. Its isolation shows clearly that C3 of the initial glucoside has undergone inversion. Fletcher and Goepf (4) have observed that hydroxyl groups may be inverted by heating a polyhydroxy compound with Raney nickel alone and then hydrogenating under normal conditions, but inversion during hydrogenolysis over copper chromium



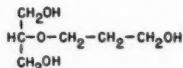
VII



VIII



IX



X

oxide has not been reported hitherto. The triol, melting point 66–69° C., could not be isolated in sufficient quantity for positive identification. It also consumed 1 mole of periodate per mole and thus may be a 2-deoxy- or 4-deoxy-1,5-anhydrohexitol produced by the inversion of one or more hydroxyl groups.

Inversion of methyl glucoside did not occur under the same conditions in the absence of hydrogen. In fact, the catalyst was discolored during this experiment and it is probable that hydrogen must be present to keep the catalyst in its active state.

In an attempt to obtain further information about other glycosides which appeared to be present in small amounts, the reaction product, obtained on hydrogenolysis at 180° and after removal of solvent and unreacted methyl glucoside, was hydrolyzed with dilute acid and then chromatographed. The major portion isolated was a mixture of polyols, but some 2-deoxy-D-glucose and smaller amounts of perhaps five or six other reducing sugars were present; the latter could not be completely separated. Although all of these compounds could not be identified, their presence suggests that inversion products other than those described above have been formed in very small amounts.

Polygalitol (1,5-anhydro-D-sorbitol) (II) was shown to be a possible intermediate reaction product in the hydrogenolysis of methyl glucoside, but one which is reduced further under the conditions of the reaction. This is suggested by the fact that a sample of polygalitol, treated under the usual conditions at 220° C., was completely converted to a mixture of polyols which was found to contain appreciable quantities of 2-hydroxy-methyl-4,5-dihydroxytetrahydropyran and hydro-D-glucal. Smaller amounts of hydro-D-altral, the unidentified isomer having melting point 66–69° C., and another unknown cyclic triol were also recovered. These results indicate also that inversion occurs after the methoxyl group of methyl glucoside has been cleaved.

The type of substituent at C1 had little influence on the course of the hydrogenolysis. Thus, the products obtained from methyl β -D-glucopyranoside and *n*-butyl α -D-glucopyranoside were qualitatively the same as that obtained from methyl α -D-glucopyranoside.

Finally, the effects of prolonged rehydrogenation were studied by subjecting the crude material obtained after 5 hours reaction time at 220° C. to hydrogenolysis at this temperature for a further 24 hours. The open-chain diols produced were separated by azeotropic distillation with naphthalene and estimated individually by the method described previously (13). The amounts of hexanediols, 1,2-propanediol, and ethanediol obtained were about the same as those recorded for the reaction at 240–250° C. The

remaining cyclic polyols were separated by distillation into more volatile polyols of R_f 0.70–0.64 which had not been found in previous hydrogenations and a higher-boiling fraction, R_f 0.48–0.42, which consisted mainly of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran.

In this work it was found also that the reaction was not noticeably affected by using ethanol instead of dioxane (2, 13) as solvent, and the former was used in all of the experiments described.

EXPERIMENTAL

Melting points are corrected and were measured with a Leitz heating stage microscope. Paper chromatograms were developed using Whatman No. 1 paper, *n*-butanol-ethanol-water (40:11:19 v/v) as solvent, and either *p*-anisidine hydrochloride (6) or silver nitrate-ammonia (10) as spray reagents. All R_f values refer to this system, and R_{rham} , R_{rib} , and R_{arab} denote the distance travelled from the starting point relative to rhamnose, ribose, and arabinose, respectively. Column chromatography was carried out on standard grade Whatman cellulose powder using about 50 g. powder per 1 g. of polyols (5). The following solvent systems were used as the mobile phase:

Solvent A: *n*-butanol, one-eighth saturated with water.

Solvent B: benzene-ethanol-water (10:1:trace, v/v).

Solvent C: benzene-ethanol-water (7:1:trace, v/v).

Solvent D: benzene-ethanol-water (5:1:trace, v/v).

Infrared spectra were recorded in the manner previously described (2, 14).

Hydrogenolysis Procedure

The same procedure as that previously described (2) was followed. Hydrogen was introduced into the bomb at 135 atmospheres (2000 p.s.i.) initial pressure. Since it was found that the use of ethanol as solvent instead of dioxane did not influence the reaction to any noticeable extent, ethanol having an average water content of 0.2% was used in all experiments.

Hydrogenolysis at 220° C. for 5 Hours

Methyl α -D-glucopyranoside, m.p. 170.5–171.5° C., $[\alpha]_D^{20} +159.4^\circ$ (H₂O) and 0.029% reducing value (2, 13), 100 g., was reacted together with copper chromium oxide, 10 g., in absolute ethanol, 1000 ml., at 220° C. for 5 hours. After removal of solvent a sirupy product, 80 g., was obtained. A portion of the sirupy reaction product, 2.0 g., was analyzed by column chromatography. The initial separation was carried out with solvent C and the first half eluted was rechromatographed with solvent B. Fraction A (0.15 g., R_f 0.75–0.65) was a mixture of open chain diols (see also below). Fraction B (0.07 g., R_f 0.52) crystallized after distillation *in vacuo*, $b_{0.15}$ 130° C. (air bath), as prisms from ether-methanol, m.p. 104–104.5° C., which were subsequently identified as hydro-D-altral (see below). Fraction C (0.10 g., R_f 0.52 and 0.60) was a mixture, and after a further amount was obtained from the hydrogenolysis at 200° C., it was fractionated on sheets of paper. About two-thirds of the material isolated, that having R_f 0.60, crystallized from acetone-ether, m.p. 88–91°. Acid hydrolysis gave a reducing sugar having the same R_f value as that of 2-deoxy-D-glucose. On admixture with an authentic specimen of methyl-2-deoxy- α -D-glucopyranoside, m.p. 88–89° C., prepared by the method of Hughes *et al.* (7), it gave m.p. 88–90° C. Fraction D (0.05 g., R_f 0.60) appeared to be mainly methyl-2-deoxy- α -D-glucopyranoside, but did not crystallize readily. Fraction E (0.39 g., R_f 0.46) was still a complex mixture containing small amounts of different glycosides. These were removed after acid hydrolysis by chromatography on a charcoal

column (15). The residual sirup gave an infrared spectrum closely resembling that of hydro-D-glucal. On seeding with hydro-D-glucal, m.p. 83–85° C., prepared by the method of Fischer (3), a portion crystallized; m.p. 82–83.5° C., mixed m.p. 81.5–84° C. Calculated for $C_6H_{12}O_4$: C, 48.64; H, 8.16%. Found, C, 48.67, H, 8.11%. Fraction F (0.20 g., R_f 0.47 and 0.37) was a mixture which could be separated partially by paper chromatography. One fraction, R_f 0.37, crystallized after distillation *in vacuo*. Prisms from ether–acetone, m.p. 66–69° C. Calculated for $C_6H_{12}O_4$: C, 48.64; H, 8.16%. Found, C, 48.68; H, 8.17%. The compound consumed 1.15 moles of periodate per mole. Its infrared spectrum resembled those of the identified tetrahydropyrantriols, but it was not similar in all respects with any one of these. Fraction G (0.18 g., R_f 0.47–0.42) was similar to fraction H, but contained impurities. Fraction H (0.25 g., R_f 0.42) on distillation *in vacuo* gave a sirup which had an infrared spectrum identical with that of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran. Fraction I (0.03 g., R_f 0.42–0.28) contained a very small amount of unreacted methyl glucoside.

Hydrogenolysis at 200° C. for 5 Hours

Analysis of the reaction product by column chromatography (solvent B) gave, in general, results similar to those above, except that only traces of open-chain diols were isolated and about one-third of the starting material was recovered. Also, a glucoside having R_f 0.52 was eluted ahead of the hydro-D-glucal fraction. It consumed 1.95 moles of periodate per mole (based on a molecular weight of 178) and gave on acid hydrolysis a reducing sugar of R_{arab} 0.9.

To obtain larger amounts of material, the crude reaction product, 50 g., was acetylated and fractionally distilled on a spinning band column. All the fractions obtained were found to be mixtures of two or more compounds. Methyl-2-deoxy- α -D-glucopyranosyl triacetate was appreciably concentrated in the more volatile fractions, $b_{0.18}$ 114–122° C. From these fractions 2-deoxy-D-glucose was isolated in about 2% over-all yield by column chromatography after the material had been deacetylated and hydrolyzed with 0.01 *N* sulphuric acid. The higher boiling fractions, $b_{0.18}$ 139–153° C., contained mainly the acetates of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran and methyl glucoside. Decomposition on a small scale appeared to occur from about 145° C. upward.

Hydrogenolysis at 180° C. for 3 Hours

Methyl glucoside, 200 g., was hydrogenated at 180° C. for 3 hours to give a product from which a large amount of unreacted methyl glucoside crystallized on cooling. This was filtered off and the filtrate was evaporated *in vacuo* at 45–50° C. A viscous sirup, 39 g., was obtained. A portion of this sirup, 10 g., was chromatographed in solvent D to give a small amount of polyols, 1.6 g., and methyl glucoside, 7.5 g. The latter fraction was hydrolyzed with *N* sulphuric acid, neutralized with barium carbonate, and then chromatographed with solvent A. Besides glucose only a very small fraction having R_f 0.25 was isolated. This was found to contain mainly unhydrolyzed methyl glucoside. Rehydrolysis and rechromatography yielded a trace, 0.027 g., of a gum having R_f 0.25 which failed to crystallize on being seeded with polygalitol (R_f 0.25–0.27). The polyol fraction was hydrolyzed with 0.01 *N* sulphuric acid for 18 hours on a steam bath, neutralized with barium carbonate, and chromatographed in solvent A. Polyols having R_f 0.64–0.33 were first eluted and then a small amount of a reducing sugar, R_{rham} 0.9, which crystallized on standing. Recrystallization from water–acetone–ethanol gave a compound of m.p. 146–148.5° C.; mixed m.p. with an authentic sample of 2-deoxy-D-glucose was 145–148° C. Furthermore, three reducing sugars were eluted, having R_{rth} 1.0, R_{arab} 1.1, and R_{arab} 0.9 respectively. Each fraction was submitted to catalyzed and

uncatalyzed lead tetraacetate oxidation (11), but the results were inconclusive and of a non-integral character. Reduction of each sugar fraction with sodium borohydride yielded products which were shown by paper chromatography to be mixtures of polyols.

Hydrogenolysis of Polygalitol

Polygalitol was obtained by lithium aluminum hydride reduction of tetraacetyl- α -D-glucopyranosyl bromide (9). The product, 1.0 g., was hydrogenated in the presence of copper chromium oxide, 0.2 g., and ethanol, 10 ml., at 180° C. for 3 hours. The starting material was recovered practically quantitatively and the catalyst was found to be reddish in color. The same results were obtained when this sample was treated similarly at 200° C., and after it had been refluxed in ethanol for several hours with excess catalyst, again at 200° C. The sample was then reacted at 220° C., in the presence of 0.6 g. catalyst, giving a product which showed (paper chromatography) no starting material. The sirupy product, 0.362 g., was chromatographed in solvent C and yielded a very small amount of a polyol having R_f 0.52 (probably hydro-D-altral); hydro-D-glucal, 0.040 g.; impure hydro-D-glucal, 0.046 g.; a mixture of polyols, 0.050 g., having R_f 0.47 and 0.37; and 2-hydroxymethyl-4,5-dihydroxytetrahydropyran, 0.057 g. Identifications were made either by mixed m.p. or by comparison of the infrared spectra with those of an authentic specimen. The mixture having R_f 0.47 and 0.37 contained a compound which gave an infrared spectrum similar to that of the tetrahydropyrantriol, m.p. 66–69° C.

Rehydrogenation

The product obtained after 3 to 5 hours reaction time at 220° C. was rehydrogenated for 24 hours at 220° C. After removal of solvent, the reaction product was distilled with excess naphthalene. The open-chain polyols were recovered by washing the distillate with water. The aqueous solution was then analyzed by partition chromatography in the manner described previously (13). The amount of naphthalene distillable material rose from about 5% to 16–25% and was found to contain isomeric hexanediols, 1,2-propanediol, and ethanediol in about the same proportion as had been found in the hydrogenolysis at 240–250° C. (13). The residue from the naphthalene distillation was further fractionated by fractional distillation *in vacuo* and countercurrent distribution, using *n*-butanol: water as solvent system. The major portion of this fraction was composed of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran (about 20–25% over-all yield), which could be isolated in a fairly pure state. The balance of material was a mixture of cyclic triols and open-chain polyols, which could not be resolved satisfactorily. One fraction appeared to be composed mainly of a hexanetriol, but it could not be obtained sufficiently pure for identification.

Rehydrogenation at 250° C. for 1 hour gave essentially the same results.

Hydro-D-altral

A quantity of the triol, m.p. 104° C., was collected from fraction B of the hydrogenolysis at 220° C. and similar fractions from the reaction at 180° and 200° C. It was also concentrated in the fractional distillation of acetates, and could be obtained fairly pure from the fraction $b_{0.18}$ 117–122° C. by column chromatography after acid hydrolysis. The over-all crude yield varied from 0.7 to 1.2%. It was purified by distillation *in vacuo*, $b_{0.18}$ 130° (air bath), and recrystallization from ether-methanol to give m.p. 104–104.5° C., $[\alpha]_D +72.6^\circ$ (*c*, 1.4, H₂O). Calculated for C₆H₁₂O₄: C, 48.64; H, 8.16%. Found C, 48.56; H, 8.13%. The triol consumed 1.12 moles of periodate per mole in 18 hours and 0.95 moles of lead tetraacetate in 1½ hours; the latter rate was about 12 times as fast as that for hydro-D-glucal under the same conditions.

*2-O-(γ -Hydroxy-*n*-propyl)-glycerol*

Periodic acid, 0.231 g., in water, 3 ml., was added to hydro-D-glucal, 0.100 g., in water, 2 ml., and kept at room temperature for 30 minutes. The solution was neutralized with an excess of barium carbonate, filtered, and treated with sodium borohydride, 0.200 g., in water, 5 ml., overnight. The excess sodium borohydride was destroyed by the addition of acetic acid. The solution was shaken with Amberlite IR-120, 5.0 g., filtered, and evaporated to dryness. Methanol was added and the solution was again evaporated to dryness, the process being repeated three times. The residue, 0.080 g., was distilled *in vacuo*, $b_{0.1}$ 150° C. (air bath), giving a colorless sirup. The latter yielded a white crystalline *p*-nitrobenzoate which, after three crystallizations from acetone-petrol (b.p. 64–66° C.), had m.p. 115.5–116.5° C. Calculated for $C_{27}H_{23}N_3O_{13}$: C, 54.28; H, 3.88%. Found: C, 54.16; H, 3.85%.

A similar degradation of the triol, m.p. 104° C., 0.100 g., yielded a colorless sirup, 0.090 g., $b_{0.1}$ 150° (air bath), which had an infrared spectrum identical to that of 2-O-(γ -hydroxy-*n*-propyl)-glycerol. It formed a white crystalline *p*-nitrobenzoate which, after two recrystallizations from acetone-petrol (64–66° C.), had m.p. 115.5–117° C., undepressed by admixture with the authentic specimen. Calculated for $C_{27}H_{23}N_3O_{13}$: C, 54.28; H, 3.88%. Found: C, 54.42; H, 3.85%.

Rotation of the Intermediate Dialdehyde

Hydro-D-glucal, 10.59 mg., was oxidized with a threefold excess of sodium metaperiodate in 1.0 ml. of water and the rotation of the resulting reaction mixture was measured at intervals. After 3 hours the specific rotation was $[\alpha]_D -0.60^\circ$, which remained unchanged after 18 hours. When the triol m.p. 104° C., 9.94 mg., was treated similarly, the rotation was $[\alpha]_D -0.61^\circ$ after 6 hours, which was unchanged after 18 hours.

Hydrogenolysis of Other Glucopyranosides

Methyl β -D-glucopyranoside and *n*-butyl α -D-glucopyranoside (12) were subjected to hydrogenolysis at 220° C. for 3 to 5 hours. Chromatographic analysis of the reaction products showed that these were qualitatively the same as that obtained from methyl α -D-glucopyranoside.

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THE PREPARATION AND SINTERING OF FINELY DIVIDED SODIUM CHLORIDE. II¹

J. B. MOFFAT² AND R. MCINTOSH

ABSTRACT

The sintering of unpacked samples of sodium chloride of high specific surface has been investigated. The sintering occurred in the presence of known pressures of water vapor and at temperatures below 70° C. The progress of the change of specific surface was followed by measuring the physical adsorption of carbon dioxide at approximately -80° C. It has been shown that an unchanging value of the surface area of a given sample exists at each relative pressure of water vapor. The area attained is independent of the number of exposures to water vapor at pressures below the final pressure. The fractional change of area of all samples in the range 35 to 80 m.²/g. depends only upon the relative pressure of water vapor. Preliminary observations of the behavior of loaded samples showed that packing the samples does not affect the character of the sintering.

A qualitative theory to account for these findings is given. It is postulated that certain ion pairs become mobile when the binding energy to the crystal is reduced by the adsorbed water. On increasing the amount of adsorbed water additional ion pairs become free to migrate and the process resulting in loss of specific surface continues to a further extent.

INTRODUCTION

In the first paper of this series (3), Craig and McIntosh reported a successful attempt to prepare sodium chloride of specific surface up to 60 m.²/g. The procedure employed was similar to that described by Lipsett, Johnson, and Maass (8), except that a range of concentrations of sodium chloride in the carrier air stream was investigated and the smaller particles were collected in an electrostatic precipitator. Similar procedures have since been employed by Young and Morrison (12) and by Van Zeggeren, Schreiber, and Benson (13). These latter authors showed that the purity of the salt was a function of the oxygen content of the carrier gas and the voltage across the alternating current precipitator. In the present work, as in the case of that done by Craig and McIntosh, no attempt has been made to obtain chemically pure sodium chloride.

Craig and McIntosh found that the preparation of sodium chloride of such large specific surface was contingent upon two factors, namely, a low concentration of sodium chloride in the carrier gas, and the anhydrous condition of carrier gas and all parts of the apparatus. If rigorous exclusion of water vapor was not achieved, sintering occurred even at room temperature. Preliminary results of sintering due to water vapor suggested that an explanation of the phenomenon might be the solubility of the solid in conjunction with the curvature of the surface (3). A long series of experiments was then begun in the hope of determining the relationship between conditions and the rate of sintering. These conditions were to include sintering in the dry state, since other investigators have used temperatures of two to three hundred degrees to reduce the area of a given sample of the salt (10). In our experience, although much effort was expended to follow the sintering under anhydrous conditions, it was not possible to prevent accidental contamination by water vapor as the sintering was followed, and our experiments have therefore been carried out using pressures of water vapor which would make accidental contamination of negligible importance.

The findings of these experiments are unexpected, and although as wide a variety of conditions as was desired was not achieved, the results are sufficiently unusual to merit

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reporting. The major discovery is that of an area for any given sample which depends upon the initial area and the relative pressure of water vapor to which the material has been exposed. A relationship between loss of area and relative pressure is also found. A qualitative theory is proposed which is consistent with the results. This theory postulates that certain sites are more susceptible than others to adsorbed water, and the molecules forming these areas migrate to positions which do not hinder the movements of additional molecules or ion-pairs. When a given type of area has been destroyed, sintering ceases, but new areas may suffer the same fate when the relative pressure is increased. The theory regards the surface layers as containing sites of various binding energies to the underlying lattice.

The literature on sintering reveals that the process of sintering has been attributed to such mechanisms of mass transport as evaporation-condensation, volume diffusion, surface diffusion, and viscous or plastic flow (7, 11, 9). From the previous work (7, 11, 9) it is readily seen that the total transfer of mass is seldom strictly accounted for by one of the above mechanisms. Furthermore, the difficulty of distinguishing which of the various mechanisms is responsible for the sintering of a given substance has yet to be overcome.

This same type of ambiguity is encountered in the present problem. It is reasonable to expect that, with the low temperatures employed here, evaporation-condensation can be ignored, as can viscous flow, if the relatively slow rate of sintering be considered (11). Nevertheless, although surface and volume diffusion may be the preponderant mechanisms, it is quite possible that plastic flow is involved to some minor extent. It will be seen later that one of the experimental findings can be explained through the mechanism of plastic flow (9).

Of interest is a paper by Burton, Cabrera, and Frank (1) which indicates, from their calculations, that the disordering of low index faces occurs at high temperatures. However, strong adsorption on the surface may cause a considerable reduction in the temperature at which sintering occurs (2). It is possible that the same mechanism may be involved in the process under study here.

Harrison, Morrison, and Rose (5) are examining the possibility that the irreversible adsorption of atmospheric gases during the preparation of sodium chloride has some influence on its surface structure. Experiments by the present authors show that the adsorption of carbon dioxide does not alter the area of the sodium chloride once it has been formed, and thus presumably the surface structure is not altered.

In considering the present study in relation to other sintering studies, it is important to note the differences which exist between the material employed and the conditions under which the sintering takes place. The course of sintering is followed in the main by changes in surface area measured by the adsorption of a gas by the sodium chloride. Some measurements of changes in density have also been performed.

EXPERIMENTAL

The finely-divided sodium chloride was prepared by electrostatic precipitation from a stream of dried air which had been passed over sodium chloride heated to about its melting point. Variations of the temperature of the oven altered the concentration in the air stream, thus producing samples of different specific surface. The precipitator was operated under voltages of about 24,000 volts per centimeter to ensure collection of the finest particles.

By this method, fine sodium chloride containing some impurity was prepared. In

order to determine the extent of the impurities, tests of nitrate and nitrite content, and ΔpH were carried out. ΔpH is defined as the pH of the solution prepared from finely-divided salt minus the pH of the solution prepared from bulk salt. The solutions were 0.1 *M* in sodium chloride. The nitrite concentration was determined from a spot test employing sulphanilic acid and α -naphthylamine, and the nitrate content using diphenylbenzidine (4). The standard solutions of nitrite and nitrate contained the same concentration of salt as the unknown solutions. The pH measurements were made with a Beckman pH meter.

The following table records some typical results of the above tests:

TABLE I

Sample No.	Wt. per cent NaNO_2	Wt. per cent NaNO_3	ΔpH
80(c)	0.0045	2.7	0.42
83(b)	0.0015	1.4	-0.75
77(a)	0.0015	2.7	-0.20
68	<0.0015	2.1	-0.10
67	<0.0015	1.4	-0.07
87(a)	0.0015	2.1	-0.32
82(c)	0.0015	1.4	-0.40
61(a)	<0.0015	2.1	-0.41
54	0.0015	1.4	-0.01

Van Zeggeren, Schreiber, and Benson (13) found that the percentage of sodium nitrate was as high as 2.0 in some cases for precipitation voltages of 15,000 volts. They found negative ΔpH 's at low precipitation voltages and that the ΔpH value reached a maximum at about 12 kv. and then decreased to zero at about 15 kv. Results of tests for purity of salt samples prepared at higher voltages are not given by these workers. From the values listed in Table I, calculations on the basis of uniform cubes as particles indicate that as high as 30% of the surface molecules might be nitrate.*

It should be noted that, in connection with the preparation of the salt, the samples as prepared, unpacked, yielded densities of the order of 0.08 to 0.1 g./cm.³

A sample of the salt which collected in the settling chamber owing to thermal precipitation was found to have negligible surface area as measured by the adsorption of carbon dioxide, yet the apparent density of the powder bed was much below that of the bulk salt, and could not be accounted for on the basis of close-packed spheres.

Precautions were taken to prevent the salt from coming into contact with the atmosphere of the room. The sodium chloride of high specific surface was transferred from the precipitator to the weighed adsorption cell in a dry box maintained at less than 3% relative humidity. The cell and sample were quickly removed to a pump and evacuated at room temperature. Loss of surface area prevented evacuation at higher temperatures. After weighing, the surface area was determined from the physical adsorption of carbon dioxide on the salt at about -80° C. It should be noted that the apparent areas as determined by the adsorption of carbon dioxide are normally smaller than those determined employing nitrogen (3).

The sample and cell were then placed in an oven, where the sample was exposed to a definite vapor pressure of water at a given temperature. These pressures were generated

*However, since van Zeggeren, Schreiber, and Benson observed X-ray lines for NaNO_3 in their preparations, it seems more likely that nitrate is present as separate particles. The discussion which is given later is based on that premise.

from the equilibrium reaction between hydrates and their anhydrous salts at fixed temperatures.

The samples were removed from the oven after periods of 1 to 2 weeks, after which their surface areas were remeasured, and the process repeated as many times as desired.

Initially attempts were made to study sintering under anhydrous conditions. The reproducibility and self-consistency of the results obtained were not good, probably owing to the difficulty of obtaining and maintaining a completely water-free system. Consequently the majority of the work was done at higher relative pressures of water vapor, which could be more readily reproduced. Some of the results obtained under the relative pressures indicated are reported in Table V.

Figure 1 illustrates the apparatus in which some preliminary experiments on sintering under load were performed. In addition to permitting a measurement of surface area without transfer of the salt, this apparatus also allowed the density to be followed during

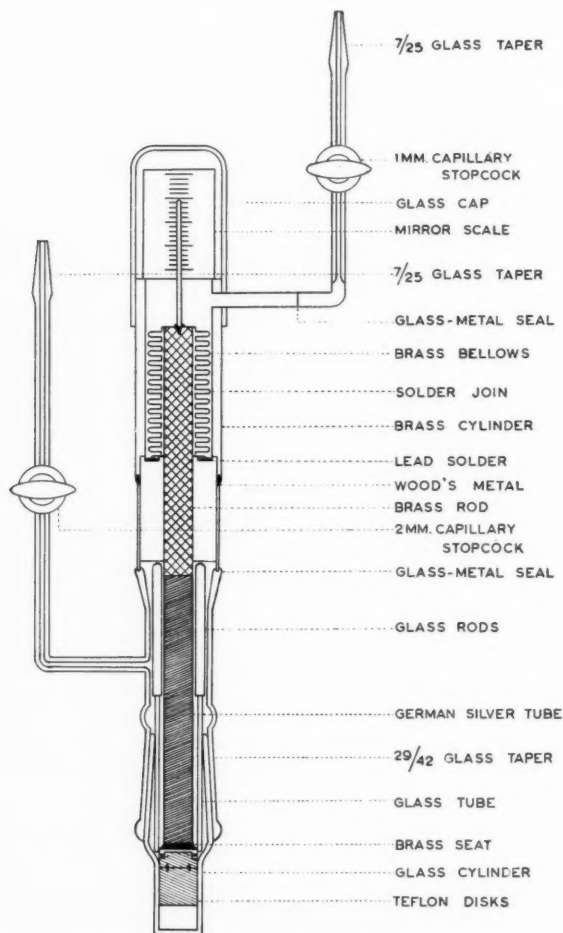


FIG. 1. Assembly for the study of packed samples aged under constant load.

the sintering process. Some difficulty was encountered with this design owing largely to the use of the brass bellows which frequently developed leaks. The presence of greased joints in this device and in the vessels ordinarily employed limited the temperature range that could be studied.

RESULTS

A number of results have been established by these experiments. First, on exposure to a given pressure of water vapor at a given temperature, the surface area of the fine salt decreases until it has reached a definite value, and then ceases to change. This is illustrated by the results found in Table II.

TABLE II

THE EXISTENCE OF A "CHARACTERISTIC AREA" OBTAINED BY EXPOSING A SAMPLE OF FINE SALT TO SOME RELATIVE PRESSURE OF WATER VAPOR

Sample number	Initial area (m. ² /g.)	Time (hr.)	Relative pressure	Temp. (° C.)	Final area (m. ² /g.)	Sample number	Initial area (m. ² /g.)	Time (hr.)	Relative pressure	Temp. (° C.)	Final area (m. ² /g.)
76(a)	33.2	121.5	0.024	55	19.2	77(b)	69.0	850	0.08	55	15.4
		183.4			19.1			1021			15.7
		272			19.0	74	74.7	823	0.024	55	33.7
53	33.6	64.3	"Dry"	92	25.5			966			33.7
		78.7			25.7			2018	0.05	41	25.8
		91.9			25.3			2197			25.9
		103.9			25.0	80(c)	85.1	1230	>0.024	55	32.8
51	34.1	90.2	"Dry"	92	23.0			1396	<0.05		33.1
		104.8			22.9			1552			32.7
76(b)	36.7	347	0.05	55	21.3	80(b)	85.2	1208	0.024	41	41.8
		445			20.5			1314			42.2
		572			20.8			1496			42.0
83(a)	48.0	1069	0.024	41	23.1	80(b)	85.2	2635	0.05	41	26.2
		1259			23.2			2877			26.2
83(b)	49.3	525	0.024	55	22.0	80(b)	85.2	3087	0.08	55	17.3
		705			22.1			3224			17.2
		909			21.7			3367			17.4
77(a)	66.1	428	0.024	55	24.3	68	87.2	47.0	0.024	55	40.6
		529			24.6			88.8			40.3
		609			23.7			137.1			40.2
		707			24.6	80(a)	87.8	612	0.012	55	57.7
59	67.3	35.1	"Dry"	92	34.0			756			58.1
		39.2			34.3			934			57.4

Second, on increasing the vapor pressure of water present, and maintaining the temperature constant, the surface area again begins to decrease until another quite definite value of the area has been attained. It appears that this process may be continued for as long as desired, or until a negligible area has been reached. Table III and Fig. 2 illustrate the effect of increasing the vapor pressure of water.

TABLE III

EFFECT OF INCREASING THE VAPOR PRESSURE OF WATER

Initial area	Final area at 2.8 mm. and 55° C. (rel. p 0.024)	Final area at 5.9 mm. and 55° C. (rel. p 0.05)	Final area at 9.1 mm. and 55° C. (rel. p 0.08)
33.2	19.1	17.2	
49.3	21.9		11.4
66.1	24.3	20.0	
85.1	32.9		15.6
87.8	43.7		16.6

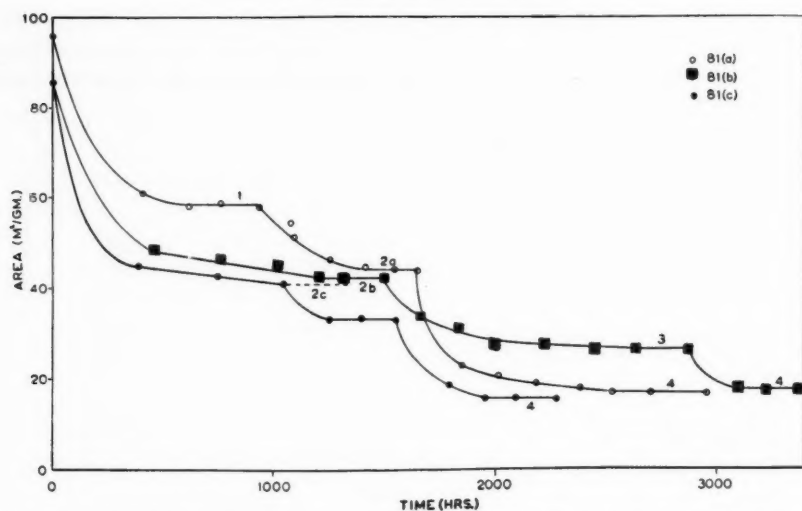


FIG. 2. Characteristic data showing metastable areas. Data also illustrate that area depends only upon p/p_0 .

Third, the results obtained show that, for temperatures of 41° C. and 55° C., the value of the surface area obtained is dependent on the relative pressure, rather than the absolute pressure. This was shown by dividing a sample of fine salt into three portions, and exposing two of these portions to the same absolute vapor pressure of water, but different relative pressures (by maintaining the two parts under the same pressure of water vapor but at different temperatures). The third portion was exposed to a different absolute pressure than that employed for the first two portions, but the same relative pressure as used for either of the first parts of the sample. Representative values from this type of experiment are recorded in Table IV. One sample was split into three portions of

TABLE IV
DEPENDENCE OF AREA ON RELATIVE, RATHER THAN ABSOLUTE,
PRESSURE OF WATER VAPOR

Initial area (m. ² /g.)	Absolute pressure (mm. Hg)	Temperature (° C.)	Relative pressure	Area (m. ² /g.)
48.0	1.4	41	0.024	23.1
49.2	1.4	55	0.012	29.5
49.3	2.8	55	0.024	21.9
85.2	1.4	41	0.024	42.0
87.8	1.4	55	0.012	57.4
87.8	2.8	55	0.024	43.7

areas 87.8, 85.2, and 87.8 m.²/g. The parts were exposed to 1.4, 1.4, and 2.8 mm. of water vapor respectively at temperatures such that the relative pressures obtained were 0.012, 0.024, and 0.024 respectively. In the same order the areas obtained were 57.4, 42.0, and 43.7 m.²/g. The error which is estimated in the measurement of surface area is ± 0.5 m.²/g. Thus the values of the areas obtained at the same relative pressure agree

closely within experimental error, whereas the areas obtained from exposure of the two parts to the same absolute pressure differ by about 15 m.²/g.

A fourth fact which was established is that the value of area attained at a given vapor pressure of water at a given temperature does not depend on the number of steps taken in reaching the final relative pressure. A sample may be brought to its characteristic area at a given relative pressure by simply exposing the sample to this relative pressure of water vapor. Alternatively, the sample may be exposed to a small relative pressure of water vapor, and an area obtained at this pressure; then by increasing the relative pressure, another value of area may be obtained until finally the sample is exposed to the desired relative pressure. The same area is obtained by this method as is found in the one-stage method. Typical data are given in Table V. This table lists the initial areas,

TABLE V
INDEPENDENCE OF AREA AND NUMBER OF STEPS INVOLVED IN PROCESS*

Initial area (m. ² /g.)	Final relative pressure	Area obtained by particular process	Area obtained by particular process
48.0	0.05	15.4''	
49.2	0.05		16.6''
66.1	0.05		19.8''
69.0	0.05	19.3'	
85.1	0.024	42.0'	
87.8	0.024		43.7'
85.1	0.08		15.6''
87.8	0.08	16.6'''	

* ' signifies that only one relative pressure of water vapor was employed in attaining that area.

'' signifies two relative pressures employed.

''' signifies three relative pressures employed.

the final relative pressure to which the sample is exposed, and the area obtained by each of two paths. The symbol ' following an area denotes that this area has been obtained by a one-step process, that is, the sample was simply exposed to the desired relative pressure immediately, without passing through any preliminary stages; the symbol '' indicates two stages, and so on.

Fifth, the preliminary experiments on sintering under load indicate that the course of sintering is not appreciably altered, at least under loads up to 0.3 atm. Experiments were begun on three samples of fine salt. The first sample, of initial area 71.0 m.²/g., was loaded to a pressure of 0.15 atm. After exposure to a relative pressure of water vapor of 0.012 for about 1300 hours it had decreased to an area of 46.0 m.²/g., at which point the area appeared to be constant. The fractional change of area equals about 0.35, which agrees well with the other fractional changes at the same relative pressure, as will be mentioned shortly (see Table VI).

The second and third samples had areas of 40.2 and 41.0 m.²/g. respectively and were exposed to a relative pressure of 0.08 under loads of 0.15 atm. and 0.3 atm. respectively. After approximately 200 hours the areas were 17.6 and 17.8 m.²/g., which appears to indicate that the effect of doubling the load on the salt is not appreciable. In all cases the areas of the samples appear to be following curves of surface area versus time similar to those obtained for unloaded samples.

A sixth point established is that the fractional change of surface area is not dependent

TABLE VI

THE FOLLOWING TYPICAL DATA ILLUSTRATE THAT FRACTIONAL CHANGES OF AREA ARE INDEPENDENT OF INITIAL AREA AND DEPENDENT ONLY ON RELATIVE PRESSURE

Initial area (m. ² /g.)	Relative pressure	Temperature (° C.)	$-\frac{\Delta A}{A}$	Initial area (m. ² /g.)	Relative pressure	Temperature (° C.)	$-\frac{\Delta A}{A}$
32.7	"Dry"	92	0.39	87.2	0.024	55	0.54
33.6			0.24	87.8			0.50
34.1			0.33	48.0			0.68
67.3			0.34	49.2			0.66
68.2			0.44	66.1			0.70
21.0	0.012	55	0.35*	69.0	0.05	55	0.72
49.2			0.40	74.7			0.66
87.8			0.34	85.2			0.69
48.0			0.52	87.2			0.72
49.3			0.55	49.3	0.08	55	0.77
53.8	0.024	55	0.52	69.0			0.78
74.7			0.55	85.1			0.81
85.1			0.52	85.2			0.80
85.2			0.51	87.8			0.81

*Incomplete experiment on loaded sample.

on the initial area, but on the relative pressure of water vapor present. Some representative data are given in Table VI and Fig. 3. It should be noted that this applies to a

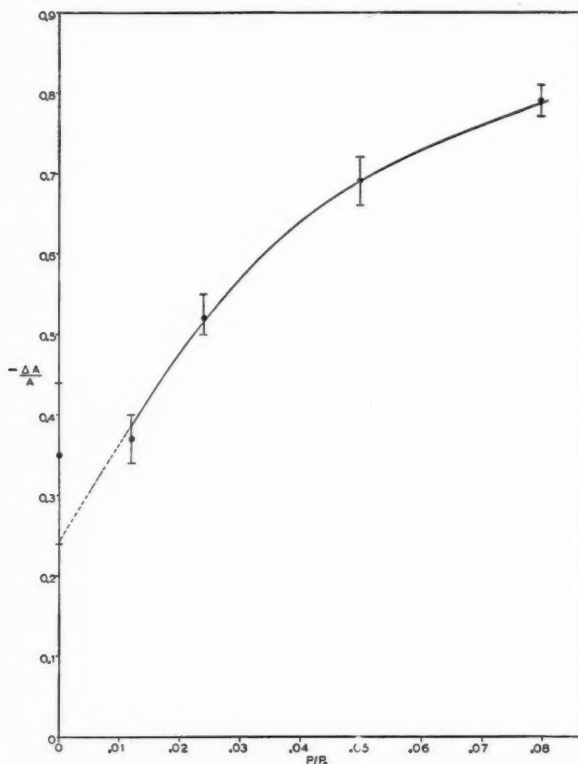


FIG. 3. $-\Delta A/A$ as a function of p/p_0 . The limits of the variation for all samples are indicated by the limits of the vertical lines.

range of areas from 40 m.²/g. to 85 m.²/g. For samples of salt having areas 35 m.²/g. and lower, there are indications that some modification of the above statement may have to be made. The electron photomicrographs obtained by Craig and McIntosh (3) indicate that the well-defined cubic structure of material of specific surface less than 35 m.²/g. may not exist in samples of the higher specific surfaces investigated here.

Harrison, Morrison, and Rose (5) examined sodium chloride of B.E.T. surface from 20 to 40 m.²/g. as determined from the adsorption of nitrogen. Under the electron microscope these particles appeared as well-formed cubes. This is seen to be consistent with the results obtained by Craig and McIntosh, if the afore-mentioned differences in apparent surface areas as determined from the adsorption of nitrogen and carbon dioxide are considered. Electron micrographs of a sample of about 50 m.²/g. obtained by Craig and McIntosh (3) show that the well-formed cubes no longer are present.

DISCUSSION

The shape of the particles of finely divided salt must be such as to provide an open network in the powder compact in order to account for the low density of the salt beds. Further, negligible adsorption of carbon dioxide by salt taken from the thermal settling chamber, yet a low density of the same salt, indicates that the particle is probably of a shape such that, although large changes of surface area are encountered on sintering, the void volume is still largely retained.

Some indication of the change of the ratio of surface area to density as a function of time is given in Table VII. This table illustrates the variation of area and density

TABLE VII

Sample number	Time (hours)	Area (m. ² /g.)	Density (g./cc.)
82(b)	0	71.0	0.097
	481.8	53.6	0.160
	788.5	50.6	0.169
	933.0	48.5	0.170
	1071	47.9	0.172
	1248	46.0	0.172
85(a)	0	40.2	0.150
	206.7	17.6	0.340
	358.5	16.9	0.346
87(a)	0	41.0	0.214
	148.8	17.8	0.396

with time for each of three samples. As is the case for samples 85(a) and 87(a), even when the surface area has become relatively small, here about 17 m.²/g., the density is still only about 0.35 g./cm.³ or approximately one-sixth of the bulk density of salt.

One shape capable of contributing some of the above properties to the sample is similar to that of a tree. It is considered that the small, fine branches, being many in number, contribute the larger part of the surface area. The thicker appendages, being sturdier, support other particles, and thus provide sufficient void volume to account for the low density.

As has been mentioned earlier in this paper, the most important fact that has been established is that of the existence of an area dependent upon the relative pressure of water vapor. In developing a theory consistent with the data this fact must first be considered.

One mechanism which might account for the above observation is that of plastic flow. Plastic flow is a mechanism of mass transport which is operative in a substance

commonly referred to as a Bingham solid, in which a yield point exists. However, it is difficult to explain, with this mechanism, any further decrease in specific surface on increase of the vapor pressure of water. If, as Herring (6) asserts, plastic flow is due to dislocations in the particle, then it is necessary that, once the original dislocations are destroyed, new ones must be created. Further, since these new dislocations are formed on the surface, it is required that they pass through the particle, unhindered, to another surface.

In the qualitative treatment to be developed here, it is postulated that in some manner the sodium chloride molecules are loosened from the surface by the water molecules adsorbed there. To account for the observed cessation of sintering at a fixed relative pressure, it must be presumed that there exist, on the surface of the sodium chloride particles, ion pairs of sodium chloride bound to the particle with various binding energies. Further, only those ion pairs bound with certain binding energies are susceptible to the water vapor at the particular value of relative pressure. Thus, on the destruction of these sites, the ion pairs having migrated to low energy points, the sintering ceases until the relative pressure is increased.

It is interesting to note that Harrison, Morrison, and Rose (5) found an initial rapid reaction in the exchange of chlorine with the surface. In addition, a comparison of the surface exchanged with the B.E.T. surface appears to indicate that the entire surface takes part in this initial reaction. From reactions observed on raising the temperature, it is considered either that the activation energy for migration of vacancies is lower for the first few layers than for the bulk or that chlorine is penetrating into the lattice. The former conclusion is consistent with the theory proposed in this paper for the sintering of the salt.

Sites with a higher binding energy become mobile at the new value of relative pressure, and the process begins again until the annihilation of these is complete. Since adsorption of water increases with increasing relative pressure, it is clear that the types of molecule which successively become mobile with increasing relative pressure require the presence of a successively larger number of water molecules in their vicinity before migration may begin. The first three experimental facts are obviously consistent with this view.

The fact that the area attained at a given relative pressure is independent of the number of steps involved may be made consistent with the theory proposed when a further assumption is made. On migration under the influence of a low relative pressure of water vapor, the migrant molecules or ion pairs cannot establish themselves in any site or energy level which would stabilize some region that would otherwise be caused to sinter by the further increase of the relative pressure in the subsequent steps of the reaction. If they did so stabilize some potentially unstable region, then, in the one-step and multi-step processes leading to the final configuration, a single value of that configuration, regardless of process, would appear to be unlikely.

In the qualitative theory proposed, there has been no particular emphasis placed upon points of contact between particles or between fibrils of a single particle. Although sintering is frequently considered to occur by diffusion across points of contact (7), since in certain cases evidence such as increasing electrical conductivity suggests this mode of growth to form larger particles, the preliminary observations on loaded samples do not require this hypothesis for the salt system. Although this aspect of the investigation has not been thoroughly developed, present information suggests that variation of the number of points of contact is of secondary importance.

The observation that the fractional change of area (for samples in the 40–80 m.²/g.

range) is dependent only upon the relative pressure must, in the light of the theory postulated, be interpreted as follows. As the specific surface is increased, the mechanism of the process causing loss of area must remain unchanged. Further, the number of the ion pairs which become mobile under any given relative pressure must be proportional to the total number in the measured specific surface of the initial unsintered sample and all aspects of the situation must remain unchanged in terms of unit area of measured surface.

Finally, if the range of types of potentially unstable ion pairs or regions of the surface is presumed to be related to the curvature of the surface (or, to what might be considered as the distribution of particle sizes in the various samples), the common value of the fractional area change from sample to sample requires comment. If the experimental fact is as stated, on the assumption that the same sizes of particles occur in each sample, it follows that the ratio of the numbers of particles in any size group is simply equal to the ratio of the areas of the respective samples. This statement holds for the range of sizes affected in the experiments up to the maximum value of p/p_0 . This unexpected result might lead one to reject the view that the energy conditions which govern the mobility or non-mobility of the types of surface are in any way related to the radius of curvature of the regions. In view, however, of the fact that the various samples have impurity contents which are quite different within the range given in Table I, there seems to be no other obvious factor which would bring about variations in the stability of the surfaces.

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THE LOCATION OF THE XANTHATE GROUPS IN PARTLY SUBSTITUTED CELLULOSE XANTHATES¹

E. P. SWAN² AND C. B. PURVES

ABSTRACT

Cellulose sodium xanthates of degree of substitution (D.S.) 0.4 to 0.66 were methylated to xanthate *S*-methyl esters which were then acetylated completely, the final xanthate D.S. remaining close to the original value. Dexanthation with aqueous chlorine dioxide near pH 4.5 and -5° removed almost all of the *S*-methyl xanthate groups, but the loss of a few acetyl groups from, and the retention of 1 to 2% of sulphur in, the resulting cellulose acetate could not be avoided. The original xanthate groups were presumably represented in this acetate as unsubstituted hydroxyl groups, and these were located by standard methods involving tosylation-iodination, tritylation, and oxidations with lead tetraacetate. Xanthate groups appeared to occupy the third and sixth, but not the second, position in the cellulose, and 53 to 61% of the substituent was in the sixth or primary position; one sample of viscose was "ripened" before the cellulose sodium xanthate was isolated, and the value was 81%. The results were of a preliminary nature, because severe technical difficulties reduced their reliability.

INTRODUCTION

As noted in a recent article (14), there have been many attempts to locate the xanthate groups in a cellulose sodium xanthate, but the instability of the compound and other technical difficulties made the results uncertain. The article in question, however, demonstrated that a cellulose xanthate could be converted by reaction with methyl iodide to the much more stable cellulose *S*-methyl xanthate, which in turn could be completely acetylated. Since both the methylation and the acetylation proceeded in high yield and without significant loss of the xanthate group, attempts were made to remove the latter without disturbing the acetyl substituent. The unacetylated positions in the resulting cellulose acetate could then have been located by standard methods. These attempts, however, steadily failed to yield a sulphur-free product and steadily involved the simultaneous removal of some acetyl groups. The present article describes further experiments with the most promising selective dexanthating agents found, sodium chlorite and chlorine dioxide.

Crystalline *O*-octadecyl *S*-methyl xanthate was oxidized near room temperature with a large excess of sodium chlorite in aqueous acetone buffered to pH 4.5, and 86% of the theoretical amount of pure, crystalline octadecanol was recovered together with 7% of an orange-brown sirup containing only 2.2% of sulphur. Since the purification of the octadecanol required several recrystallizations, which undoubtedly impaired the yield, the dexanthation of the *S*-methyl xanthate to the corresponding alcohol was quantitative or nearly so. Possible by-products like octadecyl mono- or di-thiocarbonate, ROCOSCH_3 or RS-CO-SCH_3 , or sulphonic acid, RSO_3H , were accordingly formed in very small amount, if at all.

When cellulose *S*-methyl xanthate of D.S. 0.56 (S, 16%) was dexanthated with aqueous sodium chlorite in a similar way and in two stages, about 4.5 molar equivalents of the oxidant were consumed and the cellulose, recovered in 80% yield, contained 1.14% of sulphur. This amount perhaps represented the sulphur content of a closely associated

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impurity, because the product obtained by acetylating the cellulose with acetic anhydride and pyridine under conditions in which the *S*-methyl xanthate group was stable contained only 0.15% of sulphur. A fully acetylated cellulose *S*-methyl xanthate of D.S. 0.64 was then partly dexanthated in aqueous acetic acid buffered to pH 4.5 with sodium acetate, and the product, D.S. 0.33, was dialyzed in a cellophane bag against aqueous acetone (1:9). Within the analytical error, all of the thio components were retained, and this attempt to purify the product failed. A similar product swelled but did not dissolve in acetone, and could not be fractionated. In all cases, xanthate and acetyl groups were lost in approximately equal amount, as the previous authors (14) had found. Dexanthations with sodium chlorite were accordingly discontinued, and the details of these negative experiments were omitted from this article. The loss of acetyl was associated with the loss of xanthate groups, because technical cellulose acetate retained its original acetyl content of 41.7%, and also its original viscosity, when bleached in the same conditions with sodium chlorite.

Experiments with aqueous chlorine dioxide as the dexanthating agent showed that the loss of acetyl groups could be diminished by adequate buffering of the aqueous acetic acid medium to pH 4.5 and by reducing the temperature to 0° (Table I, experiment 1). Aliquots of the liquor were withdrawn and titrated iodometrically in order to follow the consumption of chlorine dioxide (Fig. 1), but the results had little accuracy

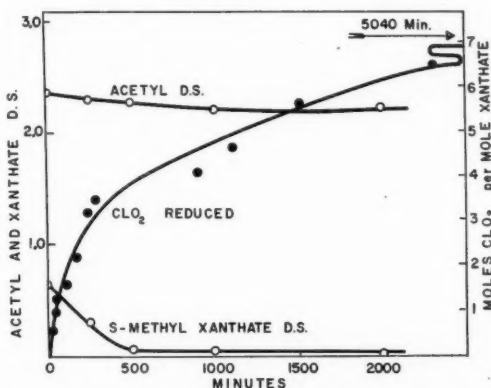


FIG. 1. Dexanthations of cellulose substituted with 2.36 acetyl and 0.64 *S*-methyl xanthate groups by excess chlorine dioxide in aqueous acetic acid buffers. Filled circles, moles of chlorine dioxide reduced per base mole of *S*-methyl xanthate at pH 4.5 and 0°; open circles, decrease in acetyl and *S*-methyl xanthate D.S. at pH 4.8 and -5°.

because no correction could be made for the decomposition of the chlorine dioxide (7) and for possible interference by thio compounds. In experiment 2 (Table I and Fig. 1) at -5° and pH 4.8, the product was isolated from four identical dexanthations at four different times. The removal of *S*-methyl xanthate groups was almost complete within 600 minutes, but at this time the loss of acetyl groups was minor. There was no advantage in extending the time of dexanthation, for a small residual content of sulphur persisted in the product, and the slow loss of acetyl groups did not cease. Subsequent experiments were carried out under the same conditions.

Experiment 3 yielded fractions A and B, which were soluble in acetone, and also the acetone-insoluble fraction C. Although the acetyl content of the three fractions differed

TABLE I
 DEXANTHATIONS OF ACETYLATED CELLULOSE *S*-METHYL XANTHATE AT -5° AND pH 4.8^a

Expt. No.	Time, hr.	Yield, ^b %	Analyses				Degree of substitution	
			% S		% OAc		Methyl xanthate	Acetyl
1	0	100	12.8	12.1	33.3	32.7	0.64	2.36 ^c
	84	98 ^d	1.3	1.2	37.0		0.05	2.10
2	4.2	95	6.8	6.8	38.5		0.30	2.31
	8.3	96	2.0	1.9	37.2	37.0	0.08	2.29
	16.6	95	1.2	1.1	36.1	37.2	0.04	2.2
	33.3	95	1.4	0.9	36.7	35.9	0.05	2.23
3 ^e	10	A 21	1.3	1.5	38.6	37.6	0.06	2.36
		B 7	1.8	1.6	37.1	37.5	0.07	2.30
		C 73	1.1	1.0	36.7	36.1	0.04	2.18
			13.2	13.2	31.2	31.6	0.66	2.32
4	0		1.8	1.6	36.1	36.1	0.07	2.18
	12		19.7	20.5	24.6	23.9	1.06	1.91
5	0	100	9.2	9.6	25.5	25.1	0.39	1.55
	10		5.5	5.6	35.0	40.5	0.26	2.62
Reacetylated ^f								

^aSolutions of 1 g. in 50 ml. of glacial acetic acid mixed with 450 ml. of aqueous 0.14 M chlorine dioxide and 100 g. of sodium acetate dihydrate.

^bCorrected for change in D.S.

^cCorrected for D.S. of 0.15 given in blank determination on the unacetylated *S*-methyl xanthate by Clark's method (3).

^dAt 0° and pH 4.5.

^eProduct separated as fractions A, B, and insoluble fraction C.

^fWith pyridine - acetic anhydride in nitrogen for 24 hours at 100°.

appreciably, all retained about the same small amount of sulphur compounds, and the attempt to eliminate these compounds failed. Fraction A was used in later work because it retained the acetyl content of the original acetylated *S*-methyl xanthate; acetyl groups might nevertheless have been lost, because this fraction might originally have been more highly substituted than the over-all average in acetyl, and lower in *S*-methyl xanthate groups. Hence, some of the later work was repeated on a similar preparation which was not fractionated (experiment 4). Experiment 5 referred to a cellulose xanthate of much higher D.S., 1.06, prepared from potassium hydroxide - cellulose. In this case even an incomplete dexanthation produced a substantial loss of acetyl groups. Reacetylation of the product with acetic anhydride and pyridine reduced the residual "xanthate" D.S. from 0.39 to 0.26.

In order to differentiate unsubstituted primary from secondary alcohol groups, the dexanthated cellulose acetate A was first tosylated and then iodinated by standard procedures (10). The cellulose acetate swelled, but did not dissolve, in the solution of *p*-toluenesulphonyl chloride (tosyl chloride) in pyridine; it was difficult to cut representative samples from the resulting hard gel, and to isolate the product promptly. These difficulties reduced the accuracy of the results, and it was also necessary to deduct the residual sulphur (1.4%) in the acetate from the sulphur content observed after tosylation. This deduction was uncertain, because the sulphur might have remained attached to the cellulose, but not as the *S*-methyl xanthate units assumed in the calculations (D.S. 0.06). The corresponding sulphur compounds might alternatively be eliminated during tosylation if they were present as impurities. When the data in columns 2 and 3 of Table II were used to calculate the acetyl D.S. during tosylation, the values fluctuated from 2.07 to 2.45 instead of staying constant at the proper D.S. of 2.36. Sulphur and tosyl contents (columns 5 and 6) therefore had to be calculated from the acetyl content

TABLE II
TOSYLATION-IODINATION OF DEXANTHATED CELLULOSE ACETATE A

Hours	Tosylation ^a				Iodination ^b			
	Obs. OAc, %	Obs. S, %	Calc. OAc, mole	Calc. S, %	Calc. Ts, %	Obs. I, %	Calc. I, mole	Secondary ^d Ts, mole
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
0	38.0	1.4	2.36	0	0	0	0	0
0.33	36.3	2.3	2.33	1.0	0.08	2.5	0.05	0.03
0.66	34.7	3.3	2.36	1.8	0.16	4.0	0.10	0.06
1.0	33.6	3.8	2.34	2.4	0.23	5.4	0.15	0.08
2	32.5	4.9	2.45	3.0	0.29	12.2	0.25	0.04
3	32.2	4.2	2.26	3.2	0.31	10.9	0.29	0.02
4	31.5	4.8	2.31	3.6	0.36	13.7	0.31	0.05
5	31.8	4.3	2.24	3.4	0.34	—	0.31	0.03
6	31.4	5.2	2.39	3.6	0.36	—	0.31	0.05
7.5	31.4	4.3	2.20	3.6	0.36	14.0	0.31	0.05
9	31.1	5.7	2.47	3.8	0.38	—	0.31	0.07
10.5	31.1	5.7	2.47	3.8	0.38	—	0.31	0.07
13	31.0	5.4	2.39	3.8	0.39	—	0.31	0.08
16.6	30.6	5.5	2.36	4.1	0.42	—	0.31	0.11
24	30.4	5.7	2.38	4.2	0.44	15.4	0.31	0.13
36	29.9	4.7	2.11	4.7	0.49	—	0.31	0.18
48	29.5	4.7	2.07	4.7	0.50	—	0.31	0.19
60	29.2	5.2	2.13	4.9	0.53	—	0.31	0.22
72	29.5	4.8	2.09	4.7	0.50	—	0.31	—
96 ^c	30.7	4.5	2.16	4.0	0.42	—	0.31	—

^a Acetate A (Table I), 5.36 g. dissolved with 26.5 g. of tosyl chloride in 90 ml. of pyridine at 25°.

^b Tosylated samples, 200 mg. or less, heated with 400 mg. of sodium iodide in 15 ml. of 2,5-hexanedione for 2 hours at 120°.

^c From column 2, assuming acetyl D.S. was always 2.36.

^d Data in column 8 subtracted from those in column 6.

^e After 5 days, S = 3.9%. After 60 days, S = 3.8, Cl = 1.65%, corresponding to D.S. 0.39 and 0.15 for tosyl and halide, respectively.

(column 2) on the assumption that the acetyl D.S. remained at its original value. Fig. 2, open and closed circles, compares the observed and the calculated sulphur contents, respectively, as tosylation proceeded. The gross deficiency in the observed values after 24 hours was caused, at least in part, by the replacement of primary tosyloxy groups by chlorine from the by-product pyridine hydrochloride.

The tosyloxy groups in the primary hydroxyl positions of the tosylated acetate A were then selectively replaced by heating with sodium iodide under suitable conditions. Although the iodine percentages (Table II, column 7, and Fig. 2, crosses) were somewhat erratic, they sufficed to show that the initial rapid replacement amounted to about 13.7%. The very slow iodination that continued after the first 4 hours was neglected. The sulphur content of the iodinated samples after deduction of the initial value of 1.4% was too small and variable to justify record. It was possible, however, to calculate the iodine substitution from the percentage, and the initial tosyl D.S., by assuming that the acetyl D.S. was always 2.36. The results (column 8) showed that close to 0.31 mole

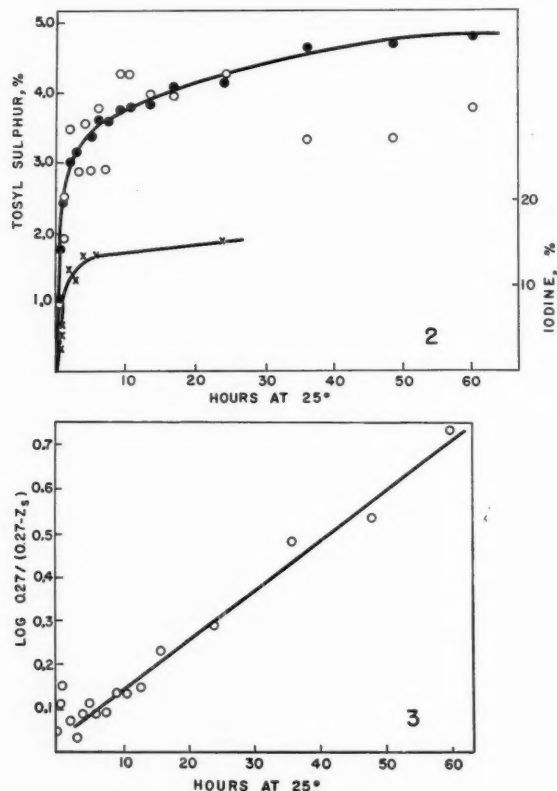


FIG. 2. Rates of tosylation and subsequent iodination of the dexanthated cellulose acetate A of Table I. Open circles, observed sulphur contents less the blank of 1.4%; filled circles, sulphur contents calculated from per cent acetyl and acetyl D.S., 2.36. Crosses and right-hand ordinates, observed iodine content. See Table II.

FIG. 3. First-order logarithmic plot of rate of tosylation of the secondary hydroxyl groups (0.27 mole) found in the dexanthated cellulose acetate A (Tables I and II).

(53%) of free hydroxyl group in the dexanthated cellulose acetate A occupied primary positions. Since the acetyl D.S. was 2.36, and the 1.4% of sulphur in the acetate A was equivalent to D.S. 0.06 as xanthate, the D.S. of unsubstituted secondary alcohol units in acetate A was, by difference, 0.27 ($3.00 - 2.36 - 0.06 - 0.31$).

Subtraction of the data in Table II, column 8, at each time from the corresponding data in column 6 gave the rate at which the 0.27 mole of free secondary hydroxyl groups was tosylated. If the amount of secondary tosylation at any time T was denoted as Z_s , then with the large excess of tosyl chloride present the first-order equation

$$KT = \log[0.27/(0.27 - Z_s)]$$

was valid (5). The values of this logarithmic function (column 10), when plotted in Fig. 3 against time, were scattered, partly because the amount of secondary tosylation during the first few hours was too small to be accurately assessed, and partly because experimental values for the iodination were used, instead of interpolated values derived from a plot. It was nevertheless evident that from 7 or 8 hours onward the points in Fig. 3 fell about a straight line that passed through, or only slightly above, the origin. Analogy with the parallel tosylation of a technical cellulose acetate (5) made it probable that this line represented the slow tosylation of hydroxyl groups in the third positions of the acetate A, and that free hydroxyl groups in the more rapidly reacting second positions were absent. The hydroxyl, *S*-methyl xanthate, or sodium xanthate substitution in the cellulose on this basis was about 0.31 in the primary or sixth position, 0.27 in the third position, and almost none in the second position, while the location of 0.06 of xanthate groups was not determined.

Since the cellulose acetate A was only a fraction of a dexanthated product, it was possibly not representative of the whole. Another tosylation-iodination was therefore carried out on the unfractionated, dexanthated cellulose *S*-methyl xanthate acetate described in Table I, experiment 4, in spite of the fact that the loss of 0.14 mole of acetyl groups this sample had incurred involved an additional error. This product had an acetyl D.S. of 2.18; the 1.7% of sulphur it retained corresponded to an *S*-methyl xanthate D.S. of 0.07, and by difference 0.75 mole of free hydroxyl group was present. The determination of the sulphur content of the partly tosylated samples was attended by the difficulties already described, and the data were omitted from this article. In brief, if the entire amount of the original sulphur was subtracted, iodination revealed a variable but slight excess of primary over total tosylation during the first few hours. This anomaly suggested that secondary hydroxyl groups were being tosylated at a rate too slow to offset a gradual elimination of the sulphur compounds originally present. The iodination, however, reached its final value of 17.0% with samples tosylated for 2, 4, and 11 hours, and the slow secondary increase noted in the previous iodination was absent. Of the 0.75 mole of free hydroxyl group in the dexanthated cellulose *S*-methyl xanthate acetate, 0.41 mole, or 55%, was primary; the remaining 0.34 mole was presumably attached to the third positions because its rate of tosylation was very slow.

Portions of the cellulose acetates which were tosylated and iodinated were also oxidized with lead tetraacetate in order to determine their content of unsubstituted 2,3-glycol groups (5). If xanthate groups in the original cellulose *S*-methyl xanthate had been distributed in random order but in equal amount between the second and third positions, the number of unsubstituted glycol groups in the dexanthated acetates would have been $(0.27/2)^2$ and $(0.34/2)^2$, or 18 and 29 mM., respectively, per base mole of the acetate (9). Less than 2 mM. was found in each case, and it appeared that the xanthation of one

of the two secondary positions made improbable the xanthation of the other position in the same glucose unit. Timell and Spurlin (16) found that a similar distribution of the substituent obtained with carboxymethylcelluloses at least up to D.S. about 1.5, and suggested that the negatively charged carboxymethyl ion repelled the approach of a negatively charged chloroacetate ion to the adjacent position of the cellulose. The same reasoning would apply to xanthation and similar substitutions involving negatively charged ions. Selective xanthation in the third, as opposed to the second, positions of cellulose, as indicated by the tosylation-iodination method, was not in conflict with the observed absence of glycol units in the derived cellulose acetate.

Selective condensation with triphenylmethyl chloride (trityl chloride) was also used to determine the number of unsubstituted primary hydroxyl groups in cellulose *S*-methyl xanthate. Of the 0.75 mole of hydroxyl group exposed by the dexanthation described in Table I, experiment 4, only 0.40 mole was tritylated (Table III). The corresponding

TABLE III
TRITYLATION OF CELLULOSE *S*-METHYL XANTHATES

Sample	Xanthate, D.S.	Tritylation				Tr, D.S.	Primary xanthate, %
		Yield, ^a %	S, %	Tr, %	Xanthate, D.S.		
From Table I							
Acetate, Expt. 4	0.75 ^b	83	29.3 ^c	26.7	—	0.40	53 ^d
Unacetylated	0.66	66	12.3	38.4	0.70	0.57	61
From a viscose							
Unripened	0.46	77	7.8	53.0	0.42	0.75	60
Ripened 3 days	0.41	72	7.6	44.6	0.42	0.66	81

^aOf theory; calc. from xanthate and trityl D.S.

^bFree hydroxyl D.S. after dexanthation.

^cPer cent acetyl.

^dCf. 55% by tosylation-iodination, while this method gave 53% for the acetate A.

fraction of primary hydroxy (or xanthate) groups, 53%, happened to be in very good agreement with the 55% found for the same sample by the tosylation-iodination method (footnote *d*) and with the corresponding value of 53% for the acetate A of Table I. The original, unacetylated cellulose *S*-methyl xanthate, from which the above dexanthated acetates were derived, became tritylated to a D.S. of 0.57. In this case the primary xanthate was obviously of D.S. $1 - 0.57$, or 0.43, and accounted for 61% of all the xanthate groups. Practically the same percentage pertained to an *S*-methyl xanthate prepared from an unripened viscose solution, but the product from the same viscose after ripening had 81% of its xanthate groups in the primary positions. This isolated result suggested that most of the groups lost in the ripening of viscose, at least in the initial stage, were from secondary positions in the cellulose, and were partly replaced by fresh xanthation in the primary positions. The present tritylation method, however, was not precise enough to study the distribution of xanthate groups during ripening in detail, because the determination of trityl was complicated by the presence of evil-smelling sulphur compounds and the yields of the purified trityl cellulose *S*-methyl xanthates were much less than theory required.

Alexsandru and Rogovin (1) previously used the tritylation method on a "cellulose *S*-methyl xanthate" analyzed by a method whose reliability was recently questioned (14). These authors found only 20% of the substituent in primary positions. The present results are in better agreement with very recent studies (12, 19) on the decomposition

of cellulose sodium xanthates in aqueous buffers. Control experiments showed that in xanthated sugars the primary xanthate groups were more stable than those in secondary positions. A kinetic interpretation of the rates of decomposition of cellulose xanthates isolated from commercial viscoses revealed them to be more highly substituted in the primary than in the secondary positions.

EXPERIMENTAL

Materials and Analytical Methods

The references cited contain the directions used in preparing the following substances: pure *O*-octadecyl *S*-methyl xanthate, melting correctly at 37–38° (17); various samples of cellulose sodium xanthate, the *S*-methyl ester, and the fully acetylated derivative of the latter, all of D.S. about 0.6 (14); and the same series, all of D.S. about 1.06, based on cellulose potassium xanthate made by the slurry method (2). One sample of the dewaxed cotton linters used in the above preparations was steeped in an excess of 4.5 *N* potassium hydroxide at –5° and was pressed to a press weight ratio of 5.6 before being aged for 3 days at room temperature. When xanthated with 24 ml. of carbon disulphide, the D.S. attained was 0.63 instead of more than unity. The effect of pressing a potassium hydroxide cellulose in lowering the D.S. of the xanthate prepared therefrom was noted elsewhere (2). Aqueous chlorine dioxide was prepared as previously described (7, 15) and, when necessary, solvents were purified by accepted methods (18).

The previous (14, 17) analytical methods were usually employed, but the most reliable determination of acetyl in the presence of the *S*-methyl xanthate group was found to be that involving the distillation of the sample from 30% aqueous chromic acid (8). Clark's distillation (3) from aqueous magnesium sulphate – sulphuric acid gave a high blank with cellulose *S*-methyl xanthate (Table I, footnote *c*). Iodine was determined by a modification of Doering's method (4), chlorine as previously described (5), and the triphenylmethyl group according to the method of Hearon, Hiatt, and Fordyce (6). With few exceptions, all analyses were carried out in duplicate.

O-Octadecyl S-Methyl Xanthate and Sodium Chlorite

A solution of 9.96 g. (111 mM.) of sodium chlorite in 50 ml. of water, adjusted to pH 4.5 with acetic acid, was slowly added to another consisting of 7.72 g. (21.4 mM.) of the *S*-methyl xanthate in 100 ml. of acetone. The oil which separated toward the end of the addition was redissolved by adding 75 ml. of acetone, and next morning the volume of the solution was made up to 250 ml. with water. A small aliquot was titrated iodometrically, and it was assumed that the residual oxidizing agent was exclusively sodium chlorite. On this basis, 4.96 moles of sodium chlorite per mole of octadecyl *S*-methyl xanthate were reduced. After the acetone was evaporated and the residual sodium chlorite reduced with an excess of sodium arsenite, the liquor was thoroughly extracted with ether and petroleum ether. The combined extracts yielded 6.71 g. (115%) of a white, crystalline mass with a sharp odor. Found: S, 2.17, 2.10%.

A solution of this product was reoxidized in the same way with 1.79 g. of sodium chlorite for 14 hours at room temperature, a further 0.70 mole of chlorite per mole of the original *S*-methyl xanthate being reduced. The product, 5.74 g. or 109% of theory, contained a little chlorine, as shown by fusion with sodium. Found: S, 1.46, 1.37%. Recrystallization from ethanol, taking as many crops as possible, yielded 4.65 g. (86%) of octadecanol melting at 52–53°, undepressed by admixture with an authentic sample of m.p. 57°. The mother liquors contained 0.49 g. (7%) of an orange-brown sirup. Found: S, 2.21, 2.19%.

Acetylated Cellulose S-Methyl Xanthate and Chlorine Dioxide

The first three experiments in Table I employed the fully acetylated cellulose *S*-methyl xanthate described in the first line and prepared from a sodium salt of D.S. 0.60. In experiment 1, a solution of about 1 g., or 0.003 mM., of the sample in 50 ml. of glacial acetic acid was slowly added with vigorous shaking at 0° to a solution of 80 g. of sodium acetate dihydrate in 450 ml. of approximately 0.14 *M* aqueous chlorine dioxide (about 60 mM.). Aliquots, 5 ml., of the resulting suspension (pH 4.5) were withdrawn at various times, acidified, and treated with an excess of potassium iodide. The liberated iodine was then titrated with 0.124 *N* sodium thiosulphate. The assumption that each mole of residual chlorine dioxide liberated 5 equivalents of iodine made it possible to follow the consumption of the oxidant (Fig. 1). After 84 hours at 0°, unused oxidant in the suspension was reduced by adding an excess of a saturated aqueous solution of sodium thiosulphate, and the product was recovered on a filter. The white fibers were well washed with water, boiled in ethanol for 5 minutes, and dried in a vacuum desiccator over phosphorus pentoxide (Table I). The values of *y*, the acetyl, and *w*, the *S*-methyl xanthate, D.S. were calculated from the simultaneous equations

$$\% \text{ acetyl} = 4300y/(162+42y+90w), \quad \% S = 6400w/(162+42y+90w).$$

In the other experiments, carried out at -5°, the pH was increased to 4.8 by increasing the amount of sodium acetate from 80 g. to 100 g. Four 1-g. samples were separately dexanthated for various times in Experiment 2, with the results plotted in Fig. 1. The total amount of the cellulose *S*-methyl xanthate acetate used in the next run was 36.6 g., and consisted of 18 parallel dexanthations on a 2-g. scale. Large amounts of chlorine dioxide could not be conveniently prepared at one time, and the dexanthation was exothermic. Each of these dexanthations employed 100 ml. of acetic acid, 450 ml. of the aqueous chlorine dioxide, and 150 g. of sodium acetate. The D.S. values of the combined product were 0.05 and 2.22 in *S*-methyl xanthate and acetyl groups, respectively, and the yield of 30.4 g. was 104% of theory. This product was extracted at room temperature with a mixture of acetone, 3000 ml. and ligroin, 300 ml., and after separation on the centrifuge the extract was diluted with 1000 ml. of ligroin to precipitate fraction A (6.5 g.). The residue from the extraction was re-extracted with 2000 ml. of acetone, and dilution of the acetone extract with 1000 ml. of ligroin separated fraction B (2.0 g.). The residual fraction C (21.6 g.) was extracted with ligroin before being dried.

Experiment 4 summarized the results of eight parallel dexanthations of 1-g. samples of another but similar acetylated cellulose *S*-methyl xanthate. The sample used in experiment 5 was prepared without pressing from a potassium hydroxide cellulose, and differed from those of lower *S*-methyl xanthate substitution in being insoluble in glacial acetic acid. This acetate was also insoluble in ethanol, ether-ethanol, acetone, benzene, chloroform, *N,N*-dimethylformamide, dimethylsulphoxide, pyridine, and saturated aqueous magnesium perchlorate. A cellulose *S*-methyl xanthate of similar D.S. when fully acetylated with sulphuric acid instead of pyridine as the catalyst (2) was soluble in chloroform and trichloroethylene.

Tosylation and Iodination of Dexanthated Acetates

Fraction A of experiment 3 (Table I), 5.36 g., was swollen overnight in 60 ml. of pure, dry pyridine. The suspension was mixed at 25° with a solution of 26.5 g. of pure tosyl chloride in 30 ml. of the pyridine, and the whole was kept at 25° in a thermostat (10). Although the cellulose acetate remained as a swollen gel, the liquid phase became red,

then violet, and finally brown over a period of days. Portions, each about 200 mg. in weight, were cut from the hard gel at various times, and were immersed in water-acetone (1:9) at -5° for 5 minutes in order to hydrolyze the excess of tosyl chloride. The sample was then ground several times in a mortar containing water and ice, was dried *in vacuo* over phosphorus pentoxide, and was swollen in acetone for several hours. After the acetone had been decanted, the product was triturated twice with ether and twice with ligroin, and was dried *in vacuo* over phosphorus pentoxide and paraffin wax. The analyses for sulphur (Table II) were by the Parr bomb semimicro method (13).

The initial sulphur content (1.4%) was subtracted from the observed values, and the differences were accepted as equivalent to the tosyl sulphur. Substitution in the simultaneous equations

$$\% S = 3200x/(167+154x+42y), \quad \% \text{ acetyl} = 4300y/(167+154x+42y),$$

permitted the calculation of x and y , the D.S. of tosyl and acetyl groups, respectively (Fig. 2, open circles). The value 167 for the base molecular weight of the cellulose assumed that residual *S*-methyl xanthate groups accounted for the 1.4% of sulphur it contained. An alternative method of calculating the tosyl D.S. was to assume that the acetyl D.S. retained its original value of 2.36 throughout the tosylation. In this case (Fig. 2, filled circles),

$$\% S = 3200x/\text{base mol. wt.} = 64x/203 \times \% \text{ acetyl}.$$

Some of the purified, tosylated samples, each 200 mg. or less, were heated for 2 hours at 120° with 15 ml. of 2,5-hexanedione containing 0.4 g. of sodium iodide. Moisture was excluded. The mixture was then poured into ice water and after isolation the iodinated product was washed several times with water, dried, and extracted with acetone, ether, and ligroin. Final drying was *in vacuo* over phosphorus pentoxide and paraffin wax. Although the products were analyzed for iodine (Table II and Fig. 2) and sulphur, the latter values were so small and erratic after correction for the 1.4% blank that they were discarded. The iodine D.S., called z , was therefore calculated from the equation

$$\% I = 12700z/[167+154(x-z)+110z+(2.36 \times 42)],$$

where x is the tosyl D.S. estimated from the smoothed tosylation plot of the sample before iodination (Fig. 2), and (2.36×42) is the contribution of the acetyl D.S. to the base molecular weight.

To avoid the difficulty of sampling the gel formed in the above tosylation, 17 samples (200 mg.) of the dexanthated cellulose acetate of experiment 4 (Table I) were tosylated individually in stoppered test tubes kept at 25° and sealed with ground-glass stoppers. A solution of pure tosyl chloride in dry pyridine was made to contain 26.5 g. in 100 ml., and 5 ml. was added to each tube. The products were isolated after various times, purified, and iodinated as already described, but yielded analytical data of lesser reliability than those previously obtained.

Oxidations with Lead Tetraacetate (5)

A 0.95-g. sample of the cellulose acetate A (Table I) was dissolved by shaking in 75 ml. of glacial acetic acid for 2 days. A 0.1 *N* solution, 25 ml., of freshly prepared lead tetraacetate in glacial acetic acid was added with shaking at zero time, and at various times thereafter 10 ml. aliquots of the mixture were titrated iodometrically. The results (Table IV) from 1 day onward were calculated according to the method of least squares

TABLE IV
 OXIDATIONS OF CELLULOSE ACETATES WITH LEAD TETRAACETATE

Days	Acetate 3 A ^a		Acetate 4 ^b	
	0.024 N Na ₂ S ₂ O ₃ , ^c ml.	Pb(OAc) ₄ used × 10 ³ , mM.	0.024 N Na ₂ S ₂ O ₃ , ^c ml.	Pb(OAc) ₄ used × 10 ³ , mM.
0	7.80	0	6.93	0
0.1	—	—	6.65	0.6
0.125	7.66	0.5	—	—
0.50	7.26	1.8	6.02	1.8
1	7.10	2.4	5.97	1.9
2	6.81	3.3	5.91	2.1
3	6.58	4.1	5.49	2.9
4	6.35	4.9	4.66	4.6
5	6.14	5.6	4.17	5.6

^aAcetate 3 A from Table I. Base mol. wt. 266, and 0.36 mM. sample.

^bAcetate 4 from Table I. Base mol. wt. 259, and 0.38 mM. sample.

^cTitration of iodine liberated after adding potassium iodide in excess.

(11), and extrapolation to zero time gave the consumption of lead tetraacetate as 1.66 mM. per base mole of the cellulose acetate. The same value was accepted as the apparent content of unsubstituted 2,3-glycol groups.

Cellulose acetate from experiment 4 (Table I) was oxidized in the same way, but did not quite dissolve in the acetic acid. The taking of representative aliquots was difficult, and the results were less accurate (Table IV). Only 0.92 mM. of glycol group per base mole of the cellulose acetate was found.

Tritylations (Table III)

The procedure was based on that of Malm, Tanghe, and Laird (10). In a typical case, that of the dexanthated cellulose acetate A (Table I), a 2.1-g. sample was kept at 70° for 24 hours in 25 ml. of dry pyridine containing 2 g. of pure trityl chloride. Acetone was then added to the mixture and the crude product was recovered on a filter. After being tritirated alternately with methanol and ether six times, the powder was dried *in vacuo* over phosphorus pentoxide. No way was found to eliminate an impurity that made the product light brown in color.

The unacetylated cellulose *S*-methyl xanthates were tritylated in the same way, except that the proportions of trityl chloride and of pyridine were approximately tripled and doubled, respectively. The products were also light brown powders.

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THE TEMPERATURE DEPENDENCE OF APPARENT DIELECTRIC CONSTANTS OF ADSORBATES ON NON-POROUS TITANIUM DIOXIDE¹

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ABSTRACT

The temperature dependence of the apparent dielectric constants of various adsorbed polar gases on finely divided, non-porous titanium dioxide has been determined. Within the experimental error, the apparent dielectric constant of the material adsorbed in the monolayer is independent of temperature. The effect of temperature on the dielectric constant for gas adsorbed beyond the monolayer depends on the adsorbate. These results have been interpreted as indicating that molecules initially adsorbed are oscillators, while those adsorbed in later stages of the adsorption process may be rotators or oscillators.

INTRODUCTION

Various investigators have derived formulae for the orientational polarization of adsorbed molecules. McIntosh, Rideal, and Snelgrove (4) showed that the orientational contribution to the total polarization of an adsorbed dipole constrained to rotate in the plane of the adsorbing surface is identical with Debye's result for dipoles free to rotate in space. For the case of a dipolar molecule which can undergo rotational oscillations in three dimensions about an equilibrium position, Kurbatov (3) established the result that although the orientation of the oscillator may make an important contribution to the measured polarization, the temperature coefficient of the orientational effect will be negligible if there is a reasonable restoring force to the equilibrium position of the oscillator with no field applied. Kurbatov also treated the case of a rotating dipolar molecule constrained to rotate within a given cone angle, for which he obtained the usual inverse temperature relationship. Snelgrove and McIntosh (8), and later Channen and McIntosh (2), applied this type of treatment to molecules constrained to move in the plane of the adsorbing surface and obtained similar results.

On the basis of these results, it should be possible to distinguish between oscillatory and rotary motion of adsorbed molecules from a study of the temperature dependence of the dielectric constant. In the former case, no temperature coefficient is to be expected, but in the latter, the normal temperature variation should be observed.

In this research, an attempt has been made to establish the mode of motion of the adsorbed molecules through the determination of the temperature dependence of the apparent dielectric constants of adsorbed films of various gases on finely divided non-porous titanium dioxide. Since the extended Böttcher treatment has appeared to be the most satisfactory method of analysis for determining the apparent dielectric constant of the adsorbed phase from the capacitance and corresponding adsorption data (2, 7), it has been used in this work. Furthermore, the apparent dielectric constants of adsorbed films computed by the extended Böttcher treatment exhibit the same type of temperature dependence as that observed in the plots of the primary data.

The adsorption of ethyl chloride, dichlorofluoromethane, and 1,1,1-difluorochloroethane on non-porous titanium dioxide was investigated, and, in general, the results are similar

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to those obtained in previous investigations (2, 10) with polar gases adsorbed on this adsorbent, in that there is an abrupt increase in the apparent polarization at the completion of the monolayer and the computed dielectric constant for matter adsorbed beyond the monolayer is somewhat below that of the liquid state.

For all the polar gases, there appears to be no temperature dependence of the polarization for quantities of gas adsorbed initially, that is gas adsorbed in the monolayer. On the basis of the models considered above, this lack of a temperature dependence indicates that the molecules initially adsorbed are rotational oscillators. The temperature dependence for gas adsorbed beyond the monolayer depends on the adsorbate. In the case of ethyl chloride, there appears to be a definite inverse temperature dependence, although it is much less than that observed for the bulk liquid, while for 1,1,1-difluorochloroethane the apparent dielectric constant appears to have no temperature coefficient over the limited temperature range of 30 degrees centigrade. The results indicate that the molecules adsorbed in multilayers are rotators in the former case, while in the latter case they are rotational oscillators.

EXPERIMENTAL

The experimental procedures used in obtaining the electrical and adsorption data were essentially those described previously (9, 10). Because of the danger of the distillation of mercury into the test cell during the prolonged periods required for an experimental run at the low temperatures employed, Hoke diaphragm valves were used instead

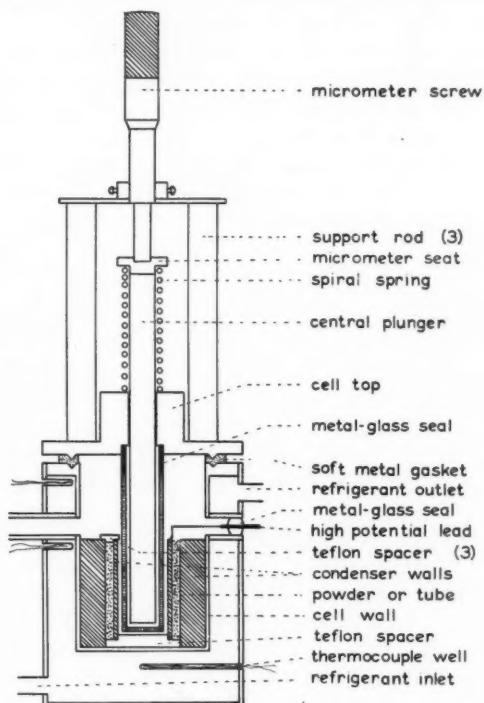


FIG. 1. Test cell and housing for high frequency measurements.

of mercury cutoffs in the adsorption assembly. These taps were of metal construction and highly resistant to corrosion. In addition, the design of the adsorption assembly was modified in order that the measuring system could be closed off from the adsorption system during the period of time required for the adsorption process to reach equilibrium. For the determination of the equilibrium vapor pressure, the vapor contained in a known volume which made up part of the adsorption system was transferred to the measuring system where the pressure could be determined. From this pressure and the values of the volumes involved, the equilibrium pressure could be determined.

The cell and housing, illustrated in Fig. 1, were similar in design to those described in detail by Waldman and McIntosh (9), but one important modification has been made. In order to eliminate the use of the teflon packing gland employed by these authors, since it frequently leaked after the temperature of the cell had been changed, a metal-to-glass seal was mounted on the cover of the housing coaxial with the two cylinders of the cylindrical condenser. The outer diameter of the metal-to-glass seal was slightly smaller than the inner diameter of the ungrounded cylinder. When the cover of the housing was in place, the glass section of the metal-to-glass seal projected down inside the inner cylinder, the ungrounded plate, almost to the lower end of the condenser. The lower end of the glass tube was sealed so that the test cell could be evacuated. Inside the metal-to-glass seal, the metal piston slid up and down forming a variable condenser with the ungrounded cylinder.

In case any dispersion in the dielectric constant of the adsorbed phase might be found with any of the adsorbates, this assembly was operated at 92.0 Mc./sec., which was the highest frequency permitting convenient operation.

Some experimental runs were carried out with the lower frequency assembly described by Waldman, Snelgrove, and McIntosh (10). All the electrical measurements obtained with this apparatus were made at the highest frequency permitted by this assembly, 3.70 Mc./sec., since no Debye-type dispersion was apparent up to this frequency.

The finely divided non-porous titanium dioxide employed as adsorbent was obtained from Dr. J. A. Morrison, of the National Research Council. Morrison, Los, and Drain (5) have reported its preparation and some of its properties.

RESULTS

Typical plots of the change in capacitance of the test cell versus quantity of gas adsorbed for ethyl chloride on non-porous titanium dioxide, at various temperatures, are illustrated in Fig. 2. Similar results were obtained with dichlorofluoromethane, in that the plots exhibit two linear sections which, when extrapolated, intersect at a critical quantity of gas adsorbed that is in good agreement with the value of the monolayer volume computed by the Brunauer, Emmett, and Teller theory (1). With both adsorbates the slopes of the second linear sections are greater than those of the first. These experimental observations are similar to those reported earlier from this laboratory (2, 10) for polar adsorbates on the non-porous adsorbent.

Corresponding plots obtained with the low frequency assembly at 3.70 Mc./sec. show the same characteristics as those in Fig. 2. In spite of the apparent similarity in the plots of the primary data obtained from the two different assemblies, the primary data cannot be compared directly, because of the difference in the geometry of the two cells involved. The dielectric constants given in Table I computed through the applications of the extended Böttcher treatment, however, show that the agreement between the dielectric constants, determined for the adsorbed phases from the electrical and adsorp-

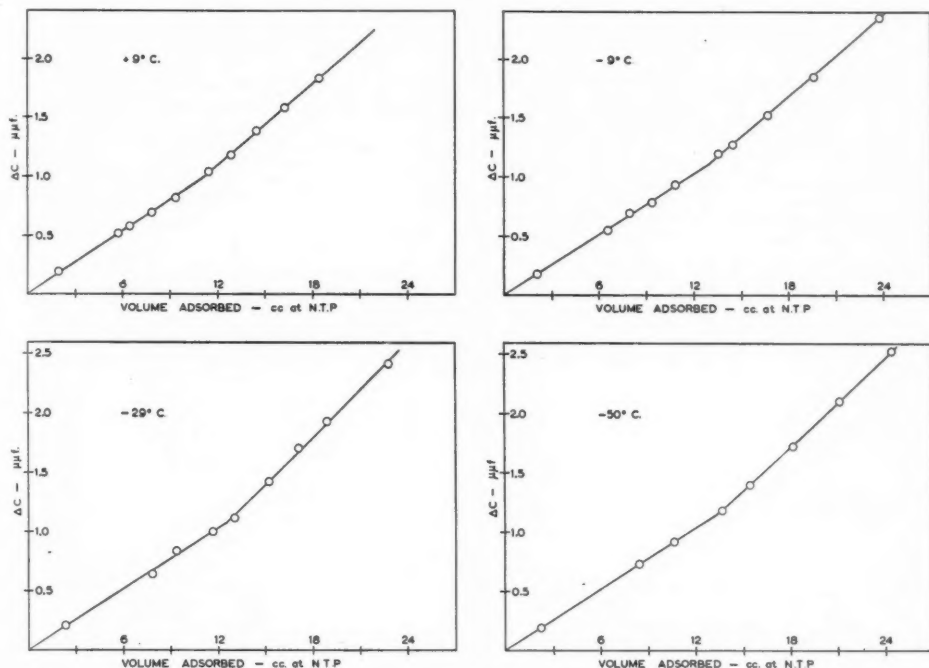


FIG. 2. Capacity change versus quantity adsorbed plots for the adsorption of ethyl chloride on non-porous titanium dioxide at 92.0 Mc./sec.

Weight of adsorbent = 1.746 g.
Cell volume = 2.42 cc.
Initial capacitance = 33.06 $\mu\mu f$.

Density of adsorbent = 4.26 g./cc.
Empty cell capacitance = 11.71 $\mu\mu f$.

tion data from the two different assemblies, is excellent. Since the geometry of the two test cells is quite different, and the volume of adsorbent involved with the one test cell is less than a third of that of the other one, the excellent agreement indicates that the extended Böttcher treatment is self-consistent.

A few experiments were carried out with 1,1,1-difluorochloroethane adsorbed on titanium dioxide with the low frequency assembly over a temperature range of approximately 30 degrees centigrade. Although the plots of capacitance change versus quantity of gas adsorbed, illustrated in Fig. 3, exhibit three linear sections, the results of these runs at -20.3°C . and -19.0°C . show that the data are completely reproducible. The slope of the first linear section is intermediate between those of the second and third sections, which have the lowest and highest slopes respectively. In view of the generality of the agreement between the positions of the discontinuities in the slopes of the plots of capacitance change versus quantity of gas adsorbed and the values of the monolayer volumes, computed from the B.E.T. equation, for polar adsorbates on titanium dioxide, the position of the second discontinuity in the slope of the plot for 1,1,1-difluorochloroethane probably marks the completion of the monolayer. On this basis, the first discontinuity, marking an abrupt decrease in apparent polarization, occurs at approximately 35% completion of the monolayer. This sudden change in the apparent polarization indicates that there is an alteration in the structure of the adsorbed film, or in the

TABLE I

DIELECTRIC CONSTANTS OF THE ADSORBED PHASE AS CALCULATED BY THE EXTENDED BÖTTCHER POWDER METHOD

Adsorbate	Temp., ° C.	Dielectric constant of the adsorbed phase			Dielectric constant of the liquid
		1st section	2nd section	3rd section	
Dichlorofluoromethane 3.70 Mc./sec. 92.0 Mc./sec.	-19.6	4.78	7.14		6.9
	+20.2	5.08	5.37		5.4
	-50.0	4.75	7.24		7.9
	-30.0	4.83	7.28		7.3
	-9.0	5.13	7.00		6.4
	0.0	5.00	5.51		6.1
	+9.0	5.30	5.30		5.9
	+9.0	5.00	5.39		5.9
	-20.3	7.87	5.60	9.01	12.4
	-19.0	7.92	5.67	9.17	12.3
1,1,1-Difluorochloroethane 3.70 Mc./sec.	-2.0	7.80	5.42	8.69	11.0
	+10.1	7.91	5.51	8.77	10.1
Ethyl chloride 92.0 Mc./sec.	-50.0	6.71	10.90		14.2
	-29.0	6.80	10.90		12.6
	-9.0	6.85	9.21		11.1
	+9.0	6.61	8.91		9.9
	+9.0	6.60	8.50		9.9

mode of motion of the adsorbed polar molecules, at this stage in the adsorption process, as a change in the internal field is unlikely, in view of the results obtained with the other polar adsorbates. The lack of information available concerning the adsorption process in the monolayer prevents one from drawing a definite conclusion regarding this phenomenon.

The dielectric constants of the adsorbed phases, given in Table I, were determined through the use of the extended Böttcher treatment, since Channen and McIntosh (2) found that although the dielectric constant computed for the bulk solid was unreasonable, the dielectric constants for the adsorbed phases, probably because of their reasonably low values, i.e., up to approximately 15, were not appreciably different from those determined by the cluster method for non-porous titanium dioxide. The extension to Böttcher's powder method depends on the volume fraction of the gas phase in the test cell, and hence, upon the density of the adsorbed phase. Thus, the dielectric constant computed for the adsorbed phase by this method depends on one arbitrary constant. The density was assumed to be that of the corresponding bulk liquid at the temperature in question.

Along with the values of the dielectric constants computed for the various adsorbed phases (Table I), the ones for the corresponding bulk liquids are listed. The values quoted for the dielectric constants of the bulk liquids, dichlorofluoromethane and 1,1,1-difluorochloroethane, were computed from the Onsager equation, and those for liquid ethyl chloride were determined by Nickerson and McIntosh (6).

Table I reveals that within the experimental error there is no temperature dependence of the dielectric constant of the first material adsorbed. In view of the discussion above regarding temperature coefficients, this result indicates that the molecules initially adsorbed are constrained to move in an oscillatory manner. These oscillators may be either planar or three-dimensional.

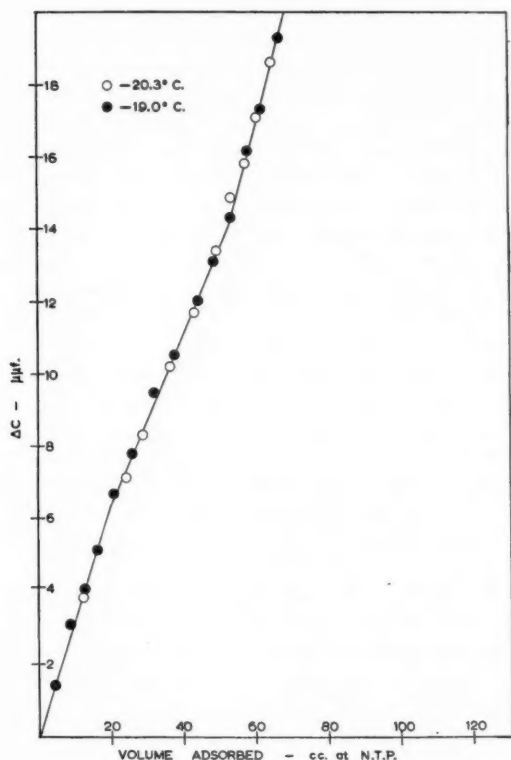


FIG. 3. Capacity change versus quantity adsorbed plots for the adsorption of 1,1,1-difluorochloroethane on non-porous titanium dioxide at 3.70 Mc./sec.

Weight of adsorbent = 6.075 g.

Cell volume = 8.56 cc.

Initial capacitance = ● 310.17 $\mu\mu\text{f.}$, ○ 313.40 $\mu\mu\text{f.}$

Density of adsorbent = 4.26 g./cc.

Empty cell capacitance = 113.90 $\mu\mu\text{f.}$

The temperature dependence of the dielectric constant of material adsorbed beyond the monolayer depends on the adsorbate. In the case of ethyl chloride, a definite temperature coefficient exists indicating rotary motion of the adsorbed molecules. The negative temperature coefficient is, however, much less than that of the bulk liquid.

Over a limited temperature range, -20.3°C. to $+10.1^{\circ}\text{C.}$, there appears to be no temperature dependence of the dielectric constants computed for 1,1,1-difluorochloroethane over any of the three linear sections. Thus, it is indicated that the mode of motion is oscillatory. If no change in the internal field or in the structure of the adsorbed film is postulated in this adsorption range, however, the mode of oscillation of the molecules initially adsorbed is different from that of the molecules adsorbed in later stages of the adsorption process.

In the case of dichlorofluoromethane, no temperature dependence of the dielectric constant for the first linear section can be detected. For the runs at -50°C. , -30°C. , -19.6°C. , and -9°C. , there appears to be no temperature dependence of the dielectric constant along the second linear section, and similarly for the runs at 0°C. , $+9^{\circ}\text{C.}$,

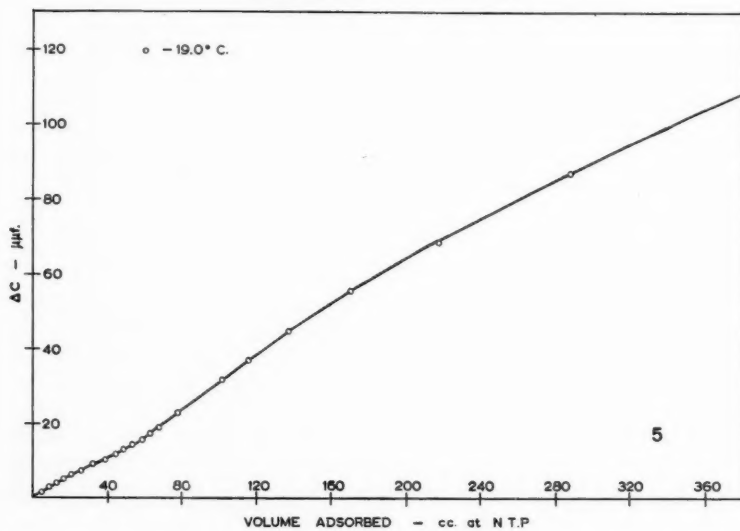
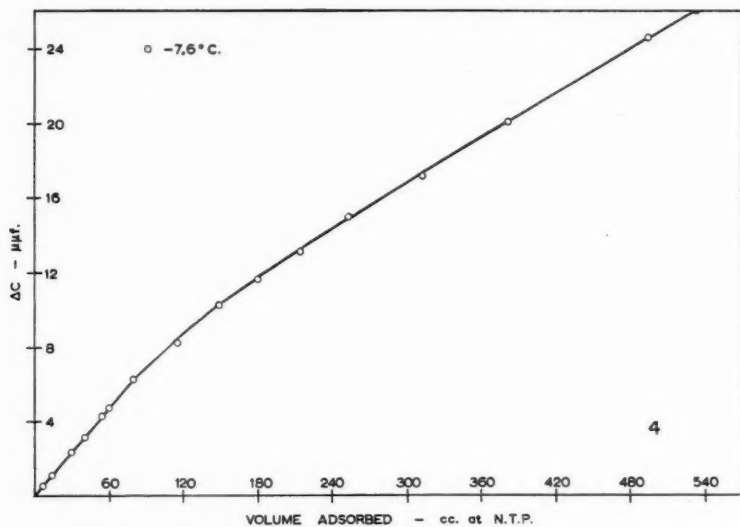


FIG. 4. Capacity change versus quantity adsorbed plot for the adsorption of *n*-butane on non-porous titanium dioxide at 3.70 Mc./sec.

Weight of adsorbent = 6.075 g.
Cell volume = 8.56 cc.
Initial capacitance = 308.70 $\mu\text{mf.}$

Density of adsorbent = 4.26 g./cc.
Empty cell capacitance = 113.90 $\mu\text{mf.}$

FIG. 5. Capacity change versus quantity adsorbed plot for the adsorption of 1,1,1-difluorochloroethane on non-porous titanium dioxide at 3.70 Mc./sec.

Weight of adsorbent = 6.075 g.
Cell volume = 8.56 cc.
Initial capacitance = 313.40 $\mu\text{mf.}$

Density of adsorbent = 4.26 g./cc.
Empty cell capacitance = 113.90 $\mu\text{mf.}$

and $+20.2^{\circ}\text{C}$. The dielectric constant of the former set, however, is considerably higher than that of the latter, i.e., 7.16 on the average as compared with 5.39 on the average. Thus, there appears to be some critical temperature between -9°C . and 0°C . at which a change in the apparent polarization occurs. Although the reason for this phenomenon is not clear, it seems established that the result obtained is real.

For both polar and non-polar adsorbates on titanium dioxide, the apparent polarization gradually decreases as adsorption proceeds after a considerable quantity has been adsorbed (see Figs. 4 and 5). As this phenomenon could be due to the formation of increasingly more dilute multilayers, at various points along the change in capacitance versus volume adsorbed plot for *n*-butane, the density of the adsorbed *n*-butane film was determined for this stage of the adsorption process in the manner proposed by McIntosh, Rideal, and Snelgrove (4). It was found that there was sufficient space in the cell to contain the adsorbate at the required densities. Therefore, the establishment of increasingly more dilute multilayers is a possible explanation for the gradual decrease in the apparent polarization of the matter adsorbed in later stages of the adsorption process. It is also possible, however, that the gradual change in the apparent polarization is the result of a corresponding gradual change in the internal field. With the information available at the present time, it seems unlikely that any conclusion regarding which of the two possible cases is involved here can be reached.

CONCLUSION

Within experimental error, the apparent dielectric constant of the material adsorbed in the first layer on non-porous titanium dioxide is independent of temperature. In view of the formulae that have been derived for the orientational polarization of adsorbed molecules, this result indicates that the molecules adsorbed initially are rotational oscillators. The temperature dependence of the dielectric constant of material adsorbed beyond the monolayer depends on the adsorbate. It has been concluded that in the case of ethyl chloride on non-porous titanium dioxide the molecules adsorbed in later stages of the adsorption process are rotators, while for 1,1,1-difluorochloroethane and dichlorofluoromethane they are probably oscillators.

ACKNOWLEDGMENTS

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ADSORPTION STUDIES ON A SERIES OF HEAT TREATED SHAWINIGAN ACETYLENE CARBON BLACKS¹

J. M. HOLMES² AND R. A. BEEBE

ABSTRACT

An experimental study has been made of the adsorption of a nitrogen, sulphur dioxide, carbon dioxide, and ammonia on Shawinigan acetylene carbon black and several derivatives of this material produced by heat treatment up to temperatures of 3000°. The effect of the heat treatment of the Shawinigan carbon black on its adsorption of the polar and non-polar gases studied is compared with the behavior of other heat treated carbon blacks. In particular, the effect of the low oxygen content of the Shawinigan black is considered. The isosteric heats of adsorption for ammonia on the most highly graphitized material (Shawinigan 3000) have been calculated. The results are in general agreement with previous calorimetric work of this laboratory. A special type of hysteresis for the system ammonia - Shawinigan black has been observed. This may be due to a reversible swelling of the graphitic material.

INTRODUCTION

For a number of years workers in the Amherst Laboratory and elsewhere have been investigating adsorption of various gases on a series of carbon blacks, chiefly channel or furnace blacks. The list of adsorbates studied has included both polar (1, 3, 5, 8) and non-polar (2, 4, 6, 7, 9, 10, 11, 19, 25) gases. Some of these investigations have been concerned in particular with the variation in adsorption isotherms and calorimetric heats of adsorption as a function of temperature of heat treatment of the adsorbents. The effect of this heat treatment on the structure of the channel and furnace blacks has been reported previously (20). It is evident that this treatment (*a*) removes oxygen complexes from the surface of the blacks and (*b*) produces a more homogeneous surface by partial graphitization of the carbon (see Table I). The presence of the latter effect has been demonstrated by electron microscopy and X-ray diffraction studies on several of the carbon blacks (20, 23, 24, 29, 30).

TABLE I
ULTIMATE ANALYSES, SURFACE AREAS, AND X-RAY ANALYSES OF GRAPHITIZED CARBON BLACKS

Sample	N ₂ surface area, m. ² /g.	X-Ray diffraction data (Å)			Percentage composition				
		<i>La</i>	<i>Lc</i>	<i>a</i>	Carbon	Ash	Hydrogen	Sulphur	Oxygen
		Data from Studebaker (27)							
Spheron (untreated)	115	22.8	13.4	—	95.14	0.08	0.60	0.25	3.94
Spheron (1000°)	91.1	36.2	15.5	7.26	99.21	0.11	0.14	0.26	0.29
Spheron (1500°)	88.0	44.8	23.3	7.03	99.72	0.08	0.02	0.09	0.10
Spheron (2000°)	85.4	75.4	41.9	6.94	99.91	0.03	0.01	0.01	0.05
Spheron (2700°)	84.1	84	48.2	6.90	99.89	0.05	0.00(3)	0.00(3)	0.06
Shawinigan (untreated)	58.0	—	—	—	99.71	0.01	0.07	0.06	0.15
Godfrey L. Cabot, Inc. (24), and Katz (16)									
Shawinigan (untreated)	58.9*	40.9	21.6	7.08	—	—	0.10	—	0.26
Shawinigan (1000°)	63.5*	40.7	21.6	7.06	—	—	—	—	—
Shawinigan (2000°)	46.9*	75.0	62.0	6.93	—	—	—	—	—
Shawinigan (3000°)	39.1*	—	76.0	6.88	—	—	—	—	—
Graphite	—	Very large		6.697	—	—	—	—	—

*Data from the present work.

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Interest in Shawinigan acetylene black has arisen because of the satisfactory properties of this black for use in dry cell batteries. This material, produced by the Shawinigan Chemicals Ltd., is prepared by the decomposition of acetylene at a temperature of about 1500° (15). In comparison with the other carbon black adsorbents, a striking property of this material is its relatively low oxygen content (27, 28). Having in mind the marked effects of the heat treatment on the adsorption of polar and non-polar gases on the channel and furnace blacks, it was decided to conduct a parallel series of studies on the Shawinigan carbon. The heat treatment and the electron microscope studies of the heat treated series were carried out in the Laboratory of Godfrey L. Cabot, Inc., of Cambridge, Massachusetts. In the present paper we are reporting the results of adsorption studies in the Amherst Laboratory on the Shawinigan blacks. In particular we have attempted to use the adsorption data for the polar gases sulphur dioxide and ammonia as a means of characterization of surface in the Shawinigan series.

EXPERIMENTAL

Materials

Ammonia and carbon dioxide of stated purity 99.9% were supplied by the Matheson Company. These gases were admitted to an evacuated system and condensed in a trap at -78°. One third of each gas was pumped out and the middle third was condensed into a second trap at -78°. From this trap one third was evaporated by pumping and the middle third was expanded into storage bulbs and in the case of ammonia into the vapor pressure thermometer. Methylamine was prepared and purified as described by Beebe and Dell (5).

Helium of 99.9% purity was passed into the storage bulbs through an activated charcoal trap immersed in liquid nitrogen. This charcoal had previously been degassed for 6 hours at 200°.

Nitrogen gas was used directly from a cylinder of 99.9% purity supplied by the Matheson Company.

The Shawinigan acetylene blacks used were supplied through the courtesy of Dr. W. R. Smith of Godfrey L. Cabot, Inc., Cambridge, Mass. The original sample (Cabot number L2463) was obtained from Shawinigan Chemicals Ltd., and is a rubber reinforcing grade black designated as 100% compressed. The other samples used were made from this original sample by heat treatment for 2 hours at 1000°, 2000°, and 3000° in an induction furnace (21). Pertinent X-ray data are shown in Table I. The a value, which is the distance in Ångström units between alternate graphitic carbon layers, serves to indicate the degree of ordering which has been achieved in the process of heat treatment. It is apparent that the a value of 6.697 Å characteristic of graphite has not been reached even at the highest temperatures of graphitization either with the Spheron channel black or with the Shawinigan black as the starting material. However, there is good evidence that fairly well ordered graphitic crystallites have been produced by the heat treatment of both materials. This conclusion is further substantiated by electron microscope data.

In Table I also are listed the analytical data for the untreated acetylene black and for the heat treated Spheron series. Ultimate analyses of these blacks have been performed by Studebaker (27, 28) and the results have been confirmed to a good approximation by the group in the Cabot Laboratory (24). Similar analyses have not been made for the heat treated acetylene blacks although the Spheron series has been analyzed. In the data of Studebaker cited in Table I, the oxygen, unlike the other elements, was

determined by difference. In a recent publication Smith *et al.* (26) have reported the direct analysis for oxygen on a sample of Graphon, which is essentially the same as Spheron (2700). Because of the direct analysis, it is probable that their average value of 0.015% oxygen is a more realistic figure than that of Studebaker.

Apparatus and Procedure

A standard volumetric adsorption apparatus using a bulb-type gas burette and a constant volume mercury manometer was used in this investigation. Pressures below 5 cm. were read with a telescope on a glass mirror scale and are estimated to be accurate to 0.1 mm.

For convenience in temperature control much of this work on ammonia and carbon dioxide has been done at about -78° using a temperature bath consisting of a large Dewar flask filled with powdered dry ice. After a preliminary adjustment period of 1-2 hours this arrangement gave a constant temperature for periods up to 48 hours, as shown by an ammonia vapor pressure thermometer. Other methods such as using dry ice in organic solvents or blowing a stream of carbon dioxide gas through a dry ice bath did not give a constant temperature over extended periods. It is advisable, if not essential, to use a vacuum-jacketed or shielded tube on the vapor pressure thermometer where it enters the cold bath to prevent local surface-cooling effects and false readings of the saturation pressure or temperature. With this temperature bath we recorded saturation pressure on an ammonia vapor pressure thermometer for each run and used this measured value for calculating relative pressure. Over a series of runs the saturation pressure of ammonia varied from about 41.1 to 41.5 mm. and on the basis of the vapor pressure of solid ammonia from International Critical Tables this gives a temperature of -78.77° to -78.73° .

For the sulphur dioxide, ammonia, and methylamine determinations at 0° an ice-water mixture was used. The saturation pressure for ammonia calculated from equations in the International Critical Tables was 321.3 cm. at the temperature of our bath, and for sulphur dioxide at 0° the saturation pressure was 116.5 cm. of mercury (5). For methylamine at 0° the saturation pressure was 100.05 cm. and for carbon dioxide at -78° a saturation pressure of 76.0 cm. was used (3). For the intermediate temperatures used for ammonia on Shawinigan (3000), freezing mixtures of chloroform, anisole, and bromobenzene gave temperatures of -64.5° , -37.4° , and -31.3° respectively. These liquids were contained in a brass cylinder around the sample in which a stirrer and heater were immersed. This cylinder was surrounded by a Dewar with dry ice-acetone mixture. Adjustment of the heater and the addition of dry ice gave adequate temperature control as recorded on the vapor pressure thermometer. Bath temperatures were calculated from the ammonia saturation pressure using the equations from International Critical Tables.

For the nitrogen isotherms, liquid nitrogen was used and its temperature was measured using an oxygen vapor pressure thermometer. Correction for the non-ideality of the unadsorbed nitrogen at the low temperature was made using the correction factor of 1.05 times the volume (S.T.P.) in the dead space when pressure is 1 atmosphere. With ammonia at -78° such corrections using the Beattie-Bridgeman equation were found to be less than 1% of the volume of unadsorbed gas at the low equilibrium pressures used and with both ammonia and sulphur dioxide at 0° the corrections for non-ideality are less than 1% for small dead spaces used in this work. Thus no corrections have been made in any of the sulphur dioxide and ammonia data for the non-ideality of the gases. With carbon dioxide and methylamine, corrections to dead space were made.

Sample bulbs of standard design were constructed to contain 1–2 g. of sample and to have a small dead space. These were connected to the measuring apparatus with 2 mm. capillary tubing but because of the light, fluffy nature of these carbon blacks a sintered glass disk was used just above the sample bulb to prevent the sample from being blown out of the bulb during outgassing.

RESULTS AND DISCUSSION

I. Nitrogen Isotherms and Surface Areas

The isotherms for adsorption of nitrogen at -195° on the untreated and the heat treated Shawinigan acetylene blacks are shown in Fig. 1. These isotherms are sigmoid

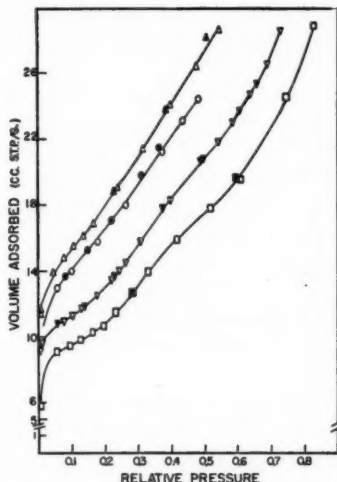


FIG. 1. Nitrogen isotherms on Shawinigan acetylene carbon blacks at -195°C . (Desorption points filled in.) \circ Untreated, \triangle Shawinigan (1000), ∇ Shawinigan (2000), \square Shawinigan (3000).

in shape (Type II), though especially in the sample heat treated at 3000° , there is a hump or change in slope of the isotherm between a relative pressure of 0.2 and 0.6. Such a hump is also evident in the 2000° treated sample, though to a lesser degree. Isotherms of similar shape on carbon adsorbents have been reported by Joyner and Emmett (14), Beebe *et al.* (4, 5), and by Polley, Schaeffer, and Smith (20) and the phenomenon is assumed to be due to lateral interaction between adsorbed molecules in the second layer. Especially with the Shawinigan (3000) the end of the hump occurs at a volume adsorbed which is about twice the monolayer volume. Much more marked stepwise isotherms have been reported by Halsey (22) and more recently in this laboratory by Beebe, Amberg, and Spencer (2).

In none of the nitrogen isotherms is there any distinct evidence of desorption hysteresis indicating the absence of pores at least in the range of pore diameter greater than 25 \AA . The Brunauer-Emmett-Teller plots of these data give good straight lines in the relative pressure range 0.05–0.25. The surface areas calculated from these B.E.T. plots are listed in Table I. It can be seen that there is a general decrease in surface area of the blacks with heat treatment except for the sample heat treated at 1000° . Polley, Schaeffer, and Smith (20) have reported a continuous decrease in surface area for the Spheron series

heat treated at successively higher temperatures. In the published data the lowest temperature of heat treatment was 1000° ; however, in a private communication Polley has informed us of work done on samples heat treated in the region of 900° . At this temperature of treatment there was a 15% increase in surface area over that of the untreated Spheron. However, if the heat treatment was conducted at 1000° , there was an abrupt decrease in area to a value less than that of the untreated material. It is probable that this initial increase in surface area followed by a sharp decrease was due to the opening up of shallow pores of small radius as a result of removal of surface oxygen during heat treatment at 900° followed by a collapse of these pores and resultant sintering of the material when the sample was heated to 1000° . We may postulate that in the case of Shawinigan black the shallow pores developed by removal of adsorbed gases, which result in increased surface area, have not been destroyed by sintering even at 1000° . It is perhaps not surprising that Shawinigan black should exhibit this difference

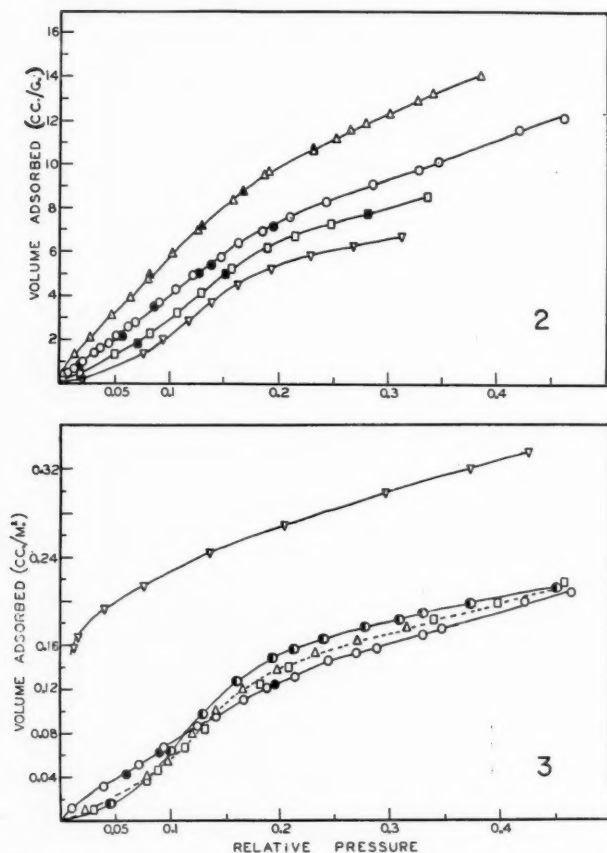


FIG. 2. Sulphur dioxide isotherms on Shawinigan acetylene carbon blacks at 0°C . (Desorption points filled in.) ○ Untreated, △ Shawinigan (1000), □ Shawinigan (2000), ▽ Shawinigan (3000).

FIG. 3. Sulphur dioxide isotherms on various heat treated carbon blacks at 0°C . Plotted on volume adsorbed per square meter of surface based on B.E.T. nitrogen area. (Desorption points filled in.) ▽ Spheron (untreated), □ Spheron (2700), ● P-33 (2700), ○ Shawinigan (untreated), △ Shawinigan (3000).

in behavior from that of Spheron owing to fundamental differences in structure and composition of these two materials.

II. Sulphur Dioxide Adsorption

The isotherms obtained for sulphur dioxide at 0° are given in Figs. 2 and 3. In Fig. 2 we have plotted the isotherms obtained on the virgin (or untreated) Shawinigan black and on the three samples derived from the virgin material by heat treatment at 1000° , 2000° , and 3000° respectively. For the purpose of comparison we have included in Fig. 3 some data taken from the work of Beebe and Dell (5) on Spheron channel black, on Spheron (2700), and on P33 (2700). In plotting Fig. 3 we have used as ordinates the volumes adsorbed per square meter of surface.* Thus due allowance has been made for any change in the extent of surface due to heating, and as a result the isotherms of Fig. 3 represent the relative adsorbability of sulphur dioxide on equal areas of the various adsorbent surfaces.

The following observations may be made about the sulphur dioxide data: (a) The isotherms were readily reproducible with no apparent change between successive runs on the same material. (b) There was no evidence of hysteresis up to the highest pressures studied. It should be noted, however, that because of experimental limitations we did not make any measurements above about 0.5 relative pressure. (c) The order of adsorptive capacity for sulphur dioxide was the same as that for nitrogen in the heat treated series, i.e. Shawinigan (1000), untreated Shawinigan, Shawinigan (2000), Shawinigan (3000). (d) With heat treatment, the low pressure portions of the isotherms changed from concave to convex with respect to the pressure axis. This effect has been observed to a much more marked degree with the heat treated Spheron series (see Beebe and Dell (5); see also Fig. 3 of this paper).

The absence of any very dramatic effect of heat treatment of the Shawinigan black on the sulphur dioxide adsorption is understandably attributable to the relatively small number of oxygen complexes on the surface of this black in comparison to Spheron 6, the surface of which is virtually covered with a monolayer of chemisorbed oxygen. Thus the chemical nature of the Shawinigan black surface undergoes relatively little change during heat treatment. The fact that the isotherm on the untreated Shawinigan sample does run slightly higher than the isotherm on its heat treated derivative can probably be attributed to the small but not entirely negligible oxygen content of the untreated surface.

For comparison, we have included the isotherm for sulphur dioxide on P33 (2700). This adsorbent has been shown from other work (2) to be even more homogeneous in surface properties than the heat treated Spheron or Shawinigan blacks. The greater trend toward an isotherm which is convex to the pressure axis on the P33 (2700) is to be expected on a more homogeneous carbon surface.

III. Carbon Dioxide Adsorption

In Fig. 4 are shown the isotherms for carbon dioxide adsorbed at -78° on virgin Shawinigan and Shawinigan (3000). For comparison the isotherm for this gas on untreated Spheron black is included. All isotherms of Fig. 4 are plotted as volume adsorbed per square meter of surface.

It is seen that carbon dioxide at -78° behaves in a manner very similar to sulphur dioxide at 0° . This result would not be expected because of the difference in polar nature of sulphur dioxide and carbon dioxide molecules. A more complete discussion of this

*The data of Table I on the specific surface areas were used in calculating these ordinates.

apparent anomaly, also observed with the heat treated Spheron series, is reported elsewhere (3).

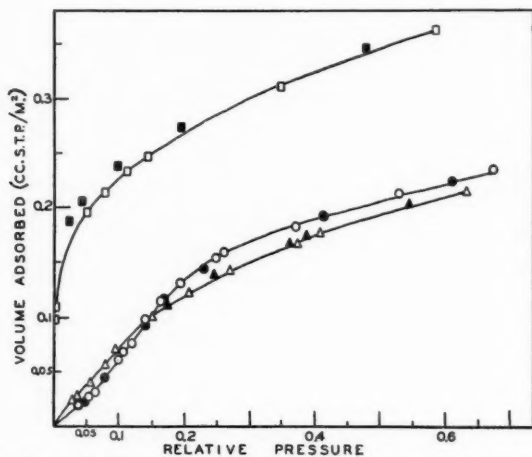


FIG. 4. Carbon dioxide isotherms on carbon blacks at -78°C . (Desorption points filled in.) \square Spheron 6, \triangle Shawinigan untreated, \circ Shawinigan (3000).

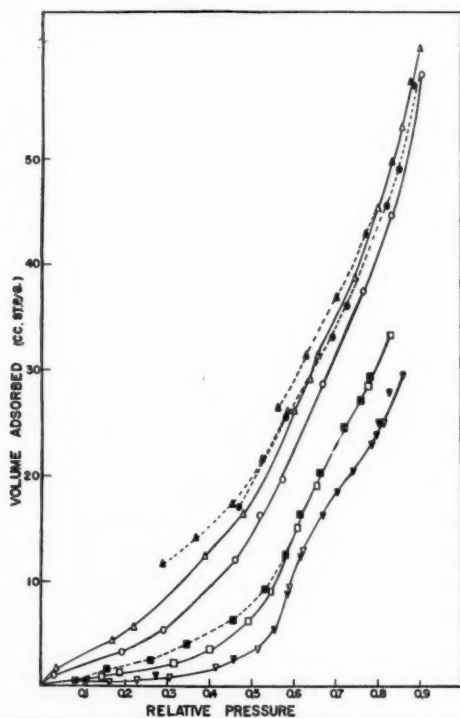


FIG. 5. Ammonia isotherms on Shawinigan acetylene blacks at -78°C . (Desorption points filled in.) \circ Untreated black, \triangle Shawinigan (1000), \square Shawinigan (2000), ∇ Shawinigan (3000).

IV. Ammonia Adsorption

(1) The Isotherms

The adsorption isotherms for ammonia on the series of Shawinigan acetylene blacks are shown in Figs. 5-9. The data at -78° on the virgin and heat treated blacks are given in Fig. 5. Adsorptions at 0° on these samples are represented in Fig. 6, and in Fig. 7 a comparison is made of the data at -78° and 0° . In Fig. 8 we have included the results of measurements at three intermediate temperatures, -31.3° , -37.4° , and -64.5° , along with the two extremes of 0° and -78° . The following points should perhaps be discussed:

(a) As with the nitrogen and sulphur dioxide, wherever check runs were made, the ammonia isotherms were reproducible. For instance, all the data shown in Figs. 8 and 9 represent agreement between two or more experiments.

(b) Unlike the nitrogen and sulphur dioxide, the ammonia did show adsorption hysteresis; this is evident from several of the isotherms and will be discussed later in a separate section.

(c) The order of adsorptive capacity for ammonia ran the same as for nitrogen and sulphur dioxide, with the Shawinigan (1000) displaying anomalously high adsorption.

(d) The shape of the ammonia isotherms in the Shawinigan series changes with heat treatment of the adsorbent. Except at relative pressures below 0.1, the ammonia isotherm is convex to the pressure axis even on the untreated material. In this respect the system ammonia-Shawinigan differs from ammonia-Spheron or sulphur dioxide-Shawinigan. It may be noted that the most drastic heat treatment of both the Spheron and the

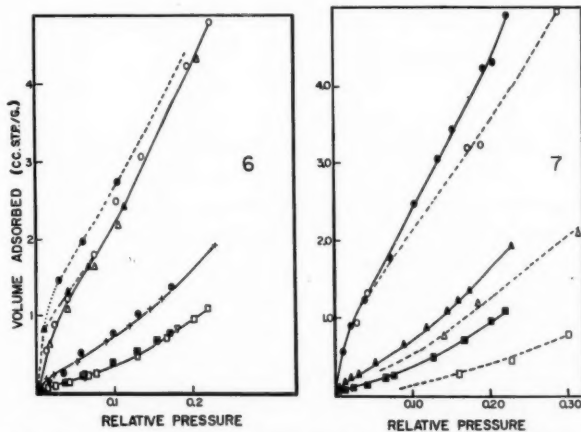


FIG. 6. Ammonia isotherms on Shawinigan acetylene blacks at 0°C . (Desorption points filled in.) Untreated Run 1 \circ , Run 2 Δ ; Shawinigan (2000) $+$; Shawinigan (3000) Run 1 \square , Run 2 ∇ .

FIG. 7. Comparison of adsorption of ammonia on Shawinigan acetylene carbon blacks at 0° and -78°C . (Solid line, 0°C ., dotted curve, -78°C .) Untreated \circ 0°C ., \bullet -78°C .; Shawinigan (3000) \square 0°C ., \blacksquare -78°C .

Shawinigan blacks results in almost identical type isotherms with a sharp rise in the region of 0.6 relative pressure. Other evidence to be published from this laboratory indicates that the presence of this rise in the ammonia isotherm is indicative of a high degree of surface homogeneity (3).

(e) Earlier work in this laboratory (5) has revealed an increase with rising tempera-

ture, in the adsorption of ammonia on graphitized Spheron carbon black, Spheron (2700). It is seen from Figs. 7 and 8 that we have observed a similar phenomenon in the present work. It is of interest that the adsorption in the ammonia-Shawinigan

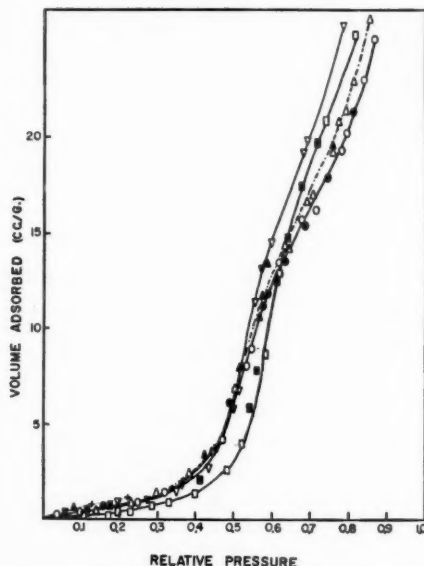


FIG. 8. Adsorption of ammonia on Shawinigan acetylene black (3000) at various temperatures. + 0°C ., \circ -31.3°C ., \triangle -37.4°C ., ∇ -64.5°C ., \square -78°C .

(3000) system shows a small but definitely positive change with temperature in the region of low relative pressure but that with the exception of the -78° isotherm, the isotherms at -31.3° , -37.4° , and -64.5° form a node at about 0.5 relative pressure and go over to the more common type of temperature dependence above this node. The -78° isotherm does not fit into this pattern. These anomalies in the effect of temperature on ammonia adsorption have been discussed and tentatively explained by Beebe and Dell (5).

(2) The Isosteric Heat of Adsorption

Beebe and Dell (5) have measured the isotherms at several temperatures for the system ammonia-Spheron (2700). These investigators have also measured the heat of adsorption for this system at -78° by direct calorimetry. The calorimetric work shows that the heat of adsorption decreases slightly from an initial value of 7.1 to 6.0 kcal./mole and then remains essentially constant (or slightly increasing) at a value of 6.1 kcal./mole, which is the heat of vaporization of ammonia at -78° ; i.e. the net heat of adsorption after the initial increments (at about 1.0 cc./g.) is virtually zero.

In spite of the uncertainties involved in applying the calculations based on the Clapeyron equation to the ammonia-carbon system, it was deemed worth while to make these calculations from the carefully measured and highly reproducible data of Fig. 8. The results are plotted in Fig. 10 and the following observations should be made:

(a) The plotted curves are based on points arbitrarily taken from the "best curves" drawn through the experimentally determined points of the isotherms. The portions

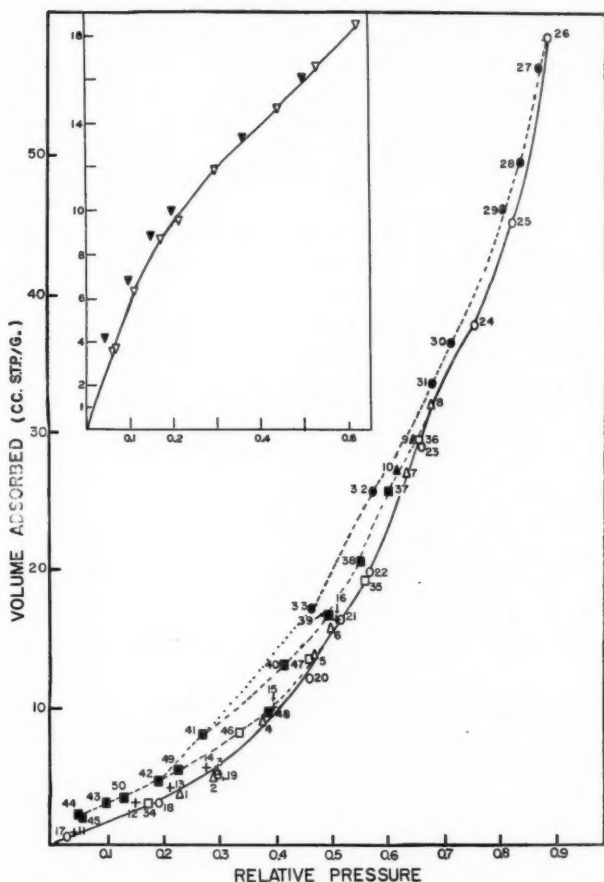


FIG. 9. Ammonia isotherms on virgin Shawinigan acetylene black at -78°C . A series of runs scanning the hysteresis loop. (Desorption points filled in.)

Δ Run 1—Points 1-8 adsorption, 9-10 desorption. (Sample pumped at room temperature before run 2.)
 $+$ Run 2—Adsorption only. Points 11-16. (Sample pumped 4 hours at 200°C .)
 \circ Run 3—Points 17-26 adsorption, 27-33 desorption. (Sample pumped 10 hours at 200°C .)
 \square Run 4—Points 34-36 adsorption, 37-45 desorption. Adsorption without pumping out, points 46, 47 followed by desorption points 48-50.

Insert: ∇ Methylamine adsorption on untreated Shawinigan black at 0°C . (Desorption points filled in.)

of Fig. 10 below about 3 cc./g. have been disregarded since the estimated percentage error is so high in reading the pressures on which the calculations are based.

(b) The isosteric heats of adsorption have been calculated by using both the integrated and differential form of the fundamental equation. There is substantial agreement of the data using both methods; in Fig. 10 we have included only the data calculated from the $\log p$ vs. $1/T$ plot, since this method is recognized as the better representation (5, 12). A large scale plot of $\log p$ vs. $1/T$ for the data in Fig. 8 resulted in a straight line relationship for the points representing data at -31.3° , -37.4° , and -64.5° but the data for -78° produced deviations in a direction which indicated higher heats of adsorption at

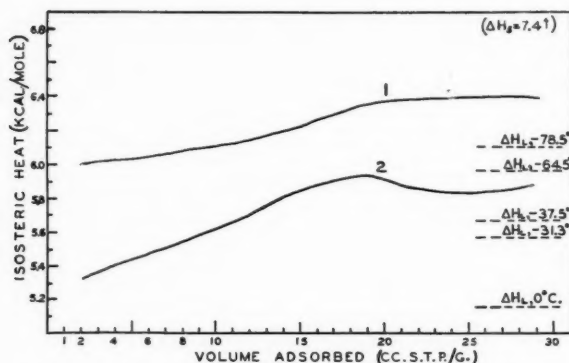


FIG. 10. Isosteric heats of adsorption for ammonia on Shawinigan acetylene black (3000) (from data in Fig. 8). Smoothed curve from plot of $\log p$ vs. $1/T$ at constant volume adsorbed. Curve 1, from data at -64.5° and -78.5° C. Curve 2, from data at -31.3° , -37.4° , and -64.5° C. (ΔH_s = Latent heat of sublimation in kcal./mole), ΔH_L = Latent heat of vaporization from work of Beebe and Dell (5).

this lowest temperature. This suggests that with Shawinigan (3000) as adsorbent, there is no marked change in the state of the adsorbed layer of ammonia in the range from -31.3° to -64.5° but that there is some rather definite change between -64.5° and -78° . It would seem that the adsorbed ammonia differs from the bulk liquid in this respect. The plots of $\log p$ vs. $1/T$ lead to heats of adsorption which are from 0.2 to 0.3 kcal. higher in the -64.5° to -78° range (curve 1) than in the -31.3° to -64.5° range (curve 2).

No evidence of anomalous behavior of isosteres in the vicinity of the monolayer volume* such as reported by Mooi, Pierce, and Smith for ethyl chloride on graphon (18) has been observed in this work. Apparent anomalous behavior of data at -78° has been referred to above but data at all other temperatures used gave isosteres as straight lines. Our temperature range is somewhat smaller than that used by Mooi *et al.* (18) and we could observe no deviations from straight line relationships in the $\log p$ vs. $1/T$ plot. An apparent maximum occurs in the isosteric heat curve at or near the monolayer volume, as might be expected.

On Fig. 10 are indicated the values of the latent heat of sublimation (ΔH_s) and the latent heat of liquefaction (ΔH_L) at the temperatures where isotherms were measured. These latent heat values are taken from the work of Beebe and Dell (5) and serve to indicate the order of magnitude of the isosteric heat of adsorption with reference to these heats. The relatively large temperature coefficient of latent heat of vaporization can be used to explain anomalies in the isotherms and in heats of adsorption, as suggested by Beebe and Dell (5).

(c) The heat data of the present work tend to confirm the calorimetric results for the ammonia-Spheron (2700) system (5) with the exception of the results at low coverage (3.0 cc./g.) where the isosteric heat values are not to be considered valid.† This is gratifying because of the rather anomalous nature of the heat curves in comparison with those for other systems reported in the literature in which the heats for the first monolayer

*The monolayer volume for ammonia has been taken as 18.7 cc. S.T.P. per gram using the value of 11.7 \AA^2 (calculated from the Emmett formula) for the cross-section of the ammonia molecule at -80° .

†In comparing the volumes adsorbed it should be borne in mind that the specific surface areas, based on nitrogen adsorption, are respectively 84.1 and 39.0 sq. m./g. for the Spheron (2700) and the Shawinigan (3000).

are usually greatly in excess of the heat of vaporization. The very limited amount of calorimetric data at 0° (5) indicates heats of the order of 5 kcal./mole. This observation of lower heats at the higher temperature is confirmed by the present isosteric heat calculations.

Because of the interesting aspects of the heat-temperature relationships brought out in the calorimetric studies and in the present work, it would be of interest to develop a calorimetric technique to determine the heats at selected intermediate temperatures over the range from 0° to -78°.

(3) *Hysteresis in the Ammonia-Shawinigan System*

It can be seen from Figs. 5, 6, and 9 that there is a definite hysteresis both at -78° and at 0° for ammonia on the Shawinigan series. This hysteresis is most pronounced on the virgin Shawinigan black and it decreases with increasing temperature of heat treatment of the carbon black. However, there appears to be a slight deviation between the adsorption and desorption isotherms even for Shawinigan (3000). Detailed data are given in Fig. 9 and the order of experiments is listed in the legend. The samples were outgassed at 200° between most runs, and at 25° between runs 1 and 2. Attention is called to the scanning of the hysteresis loop shown in Fig. 9. Analysis of the experimental details indicates that the observed hysteresis effect is real and cannot be attributed to any known experimental artifact. A similar hysteresis for adsorption of methylamine on virgin Shawinigan black is shown in the insert in Fig. 9.

In virtually all cases of hysteresis involving capillaries, the hysteresis loop closes at some point above about 0.4 relative pressure and the adsorption and desorption curves are coincident below this point. Our data do not exhibit such a closure. It is impossible to tell from the experimental data of Fig. 9 whether the desorption curve would return to the origin or whether it would give a positive intercept on the volume axis. If the latter were the case, then we would be forced to conclude that the surface itself had been altered by the adsorption of ammonia. However, any such alteration would seem to be reversible since the experimental adsorption points 46 and 47 follow a path which returns to the adsorption branch.

There is nothing very novel about a hysteresis loop of this kind so long as there is excess material of some sort on the surface of the carbon substrate (13, 19). For instance the ammonia might penetrate beneath the surface of such material with a resultant reversible swelling. It is more noteworthy if we find such a hysteresis effect on the pure carbon adsorbent resulting from heat treatment to 3000°. In work reported elsewhere (3), we have found definite evidence of such hysteresis in the system ammonia - Sterling M.T. (3100) carbon black. Such an effect may perhaps be caused by reversible swelling due to some interstitial penetration of the ammonia molecules between the graphite layers, in a manner suggested by McDermot *et al.* (17).

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CORRELATION OF O-H STRETCHING FREQUENCIES WITH pK VALUES FOR SOME PHENOLS¹

P. M. G. BAVIN² AND WILLIAM J. CANADY

ABSTRACT

The O-H stretching frequencies, in carbon disulphide, of a number of phenols have been determined. Linear relationships were observed on plotting the stretching frequency against pK_A in water. Polar substituted phenols were found to fall along one line, while phenols substituted with aliphatic groups were found to fall along another line of different slope. A change of slope is observed when the stretching frequencies of phenols are plotted against pK_A measured in alcohol-water mixtures.

Using Goulden's O-H stretching frequencies of carboxylic acids measured in carbon tetrachloride, an attempt has been made to explain the observed deviations from a single straight line in terms of electrostatic effects in the ionizing solvent. The results indicate that for the substances examined, such effects are not responsible for the observed deviations.

INTRODUCTION

Goulden (8) has measured the O-H stretching frequencies of a large number of carboxylic acids and a smaller group of phenols. The frequencies, measured in carbon tetrachloride, were plotted against the pK_A in water. It was found that all the phenols examined fell along a reasonably good single straight line. In contrast, the carboxylic acids separated into three groups when plotted in the same way, the members of each group falling along a different line. The separate plots obtained were found to be well correlated with structural characteristics of the acids in each group. The first group consisted of acids having a double bond directly attached to the α -carbon $=C-COOH$. The second group were of the $C-R_1R_2R_3COOH$ type, mainly substituted acetic acids. The third group was composed of acids in which the double bond system was separated from the carbonyl group by a methylene chain.

Three possible factors may contribute to the formation of three separate plots for the acids: (1) purely structural effects within the acid molecules themselves, (2) differences in solvent effect (solvent used for spectrophotometric analysis), (3) differences in electrostatic effects of the solvent in which the pK measurements were made. A major contribution of the second type would seem unlikely in carbon tetrachloride or carbon disulphide solutions.

The phenols examined by Goulden contained many highly polar and moderately polar substituted compounds. For this collection, the pK stretching frequency plot indicated a fairly good straight line relationship. It seemed advantageous to investigate a series of phenols containing both polar and non-polar aliphatic substituents. A complete series of monomethyl and dimethyl substituted phenols were chosen for comparison with those with polar substituents.

EXPERIMENTAL

The measurements were made with a Beckman DK-2 recording spectrophotometer using carbon disulphide as a solvent. The cell path was 1 cm. Dilute solutions of 10^{-2} to 10^{-3} molar were used to eliminate intermolecular hydrogen bonding. Wave lengths were read directly from the instrument.

The phenols showed single sharp peaks in the O-H stretching region except when intra-

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molecular hydrogen bonding was possible. Most of the phenols were commercial samples of the highest purity available, and were further purified by fractional distillation at reduced pressure or by recrystallization. *p*-Bromophenol and *p*-hydroxyacetophenone were prepared as described by Vogel (22), and recrystallized from hexane.

The O-H stretching frequencies of the phenols investigated and the pK_A values in water and in 48.9% alcohol-water solution may be seen in Table I. The O-H stretching

TABLE I

Compound	pK_A in H ₂ O at 25°	pK_A in 48.9% ethanol at 25°	O-H stretching frequency, cm. ⁻¹
1. Guaiacol	9.93 (3)		3557
2. <i>p</i> -Nitrophenol	7.14 (10)	7.68 (21)	3582
3. <i>m</i> -Nitrophenol	8.35 (10)		3586
4. <i>p</i> -Hydroxymethylbenzoate	8.47 (19)	9.58 (21)	3590
5. <i>p</i> -Hydroxyacetophenone	8.05 (2)	9.21 (21)	3591
6. β -Naphthol	9.91 (15)		3595
7. <i>p</i> -Bromophenol	9.34 (2)	10.50 (21)	3597
8. α -Naphthol	9.83 (15)		3597
9. Resorcinol	9.44 (6)		3597
10. Phenol	9.95 (10)	11.28 (21)	3600
11. Salicylaldehyde	6.79 (18)		3600
12. 3,5-Dimethylphenol	10.03 (7)		3602
13. <i>p</i> -Cresol	10.26 (1)	11.61 (21)	3604
14. <i>m</i> -Cresol	10.09 (1)	11.43 (21)	3605
15. 3,4-Dimethylphenol	10.32 (11)		3605
16. <i>o</i> -Cresol	10.29 (1)	11.55 (20)	3606
17. 2,5-Dimethylphenol	10.19 (7)		3606
18. Hydroquinone	9.96 (6)	11.78 (21)	3606
19. 2,3-Dimethylphenol	10.37 (7)		3608
20. 2,4-Dimethylphenol	10.48 (7)		3610
21. 2,6-Dimethylphenol	10.60 (23)		3618

frequencies plotted against pK_A in water are seen in Fig. 1. The data indicate that the more polar substituted phenols fall along one line, while the alkyl substituted phenols fall along a different line of smaller slope. An intimation of the same tendency may be seen in the series of phenols investigated by Goulden (8). The alkyl substituted phenols tend to deviate somewhat from the single straight line drawn. Determination of a larger number of such alkyl substituted compounds would probably have shown the existence of more than one line. Such a result is not particularly surprising in view of the three plots obtained by the same author for the three different classes of carboxylic acids. It can also be seen from Fig. 1 that ortho-methyl substituted compounds fall along a common line with meta- and para-methyl substituted compounds, and that generally non-ortho substituted methyl phenols tend to fall closer to the line formed by those with polar substituents. The substance showing the greatest deviation from this line is the highly hindered 2,6-dimethylphenol. A further indication that the two lines obtained are more than coincidental is the fact that they intersect very near phenol itself, the parent compound of both series. The line of different slope for the ortho substituted phenols is probably due to a steric effect of the ortho group on the pK_A . While ortho-, meta-, and para-methyl phenols fall along a single line, ortho substituents containing such a function as oxygen might be expected to lead to anomalies due to internal hydrogen bonding between the substituent and the hydrogen of the phenolic group. This is borne out by the fact that *o*-hydroxybenzaldehyde falls so far off the line that it has not been included in Fig. 1, although the data have been tabulated in Table I for the sake of completeness.

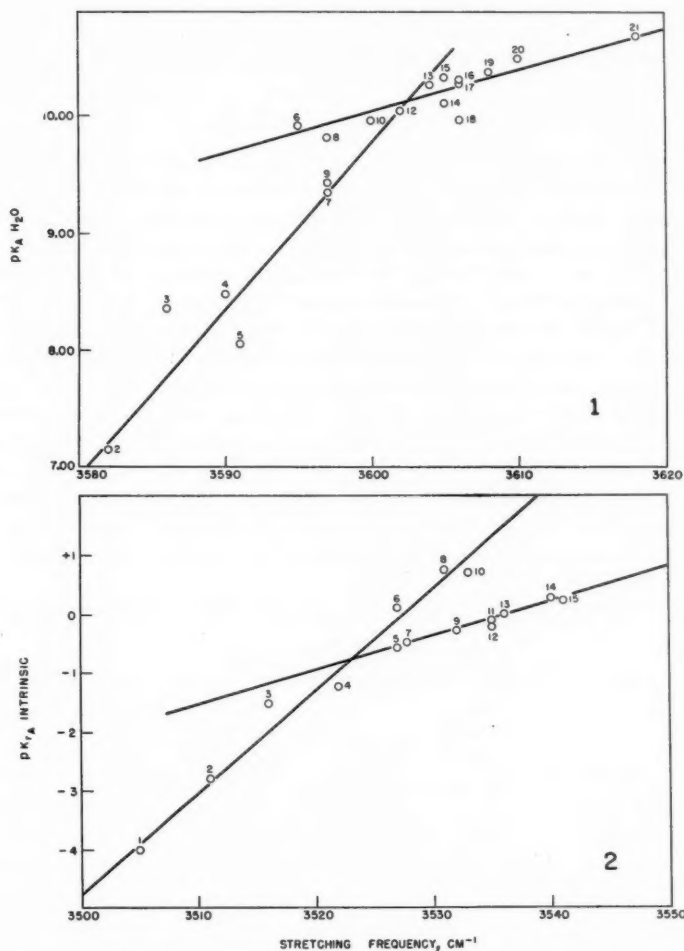
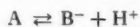


FIG. 1. O-H stretching frequencies in carbon disulphide plotted against pK_A in water. (Data from Table I.)

FIG. 2. Plot of O-H stretching frequencies against intrinsic strengths of some carboxylic acids. (Data from Table II.)

The possibility of deviation due to electrostatic effects in the ionizing solvent (water) was tested by means of a treatment due to Wynne-Jones (24). For an acid of the type

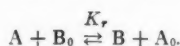


the relation will be

$$\Delta \ln K = -(\epsilon^2/2kT)[1/r_{H^+} + 1/r_B] \Delta(1/D)$$

where r_B is the radius of the anion of the acid, D is the dielectric constant of the solvent, and ϵ is the charge on the electron.

The relative dissociation constant of an acid A compared with a standard acid A_0 (K_A/K_{A_0}) is actually the constant for the equilibrium



If both the acids are uncharged as in the case of the carboxylic acids and phenols, the expression becomes

$$\Delta \ln K_{r_A} = (\epsilon^2/2kT)[1/r_0 - 1/r]\Delta(1/D). \quad [1]$$

The assumption is made that $r_A = r_B = r$, $r_{A_0} = r_{B_0} = r_0$, the ions are spherical, and the solvent is a continuous dielectric. Thus the problem of solvation of the proton is ingeniously avoided. Such a treatment is only an approximation. However, when the values of $\log K_r$ are plotted against the reciprocal of the dielectric constant, straight lines are obtained for each acid. Benzoic acid is usually selected as the standard acid, and is so used in this publication. The extrapolated intercept on the $\log K_r$ axis represents the value of $\log K_r$ in a hypothetical solvent where $1/D$ is equal to zero or where D is infinite. Such a value of K_r should be essentially devoid of electrical forces. For this reason such values have been referred to by Wynne-Jones as "intrinsic" strengths. Straight lines are obtained only when relative ionization constants are determined in pure solvents of varying dielectric constant. When mixtures such as ethanol-water or dioxane-water are used, significant curvature is noted (9). If electrostatic effects in water or aqueous mixed solvents are making contributions of varying magnitudes to the pK values of the various groups of acids, it might be expected that plotting intrinsic acid strength, which represents a purely structural free energy term, should tend to bring about a better fit to a single straight line.

Table II shows the stretching frequencies (8), relative dissociation constants in water,

TABLE II

Compound	pK_{r_A} in H_2O^*	pK_{r_A} intrinsic (infinite dielectric)	O-H stretching frequency, $cm.^{-1}$, Goulden (8)
1. Trichloroacetic	-3.90 (13)	-4.0 (24)	3505
2. Dichloroacetic	-2.91 (13)	-2.8 (24)	3511
3. Cyanoacetic	-2.77 (17)	-1.53† (16)	3516
4. Chloroacetic	-1.34 (5)	-1.24† (16)	3522
5. <i>p</i> -Nitrobenzoic	-0.78 (5)	-0.575 (12)	3527
6. Phenylacetic	+0.11 (5)	+0.1 (24)	3527
7. <i>m</i> -Nitrobenzoic	-0.71 (5)	-0.491 (12)	3528
8. Cyclohexane carboxylic	+0.67 (5)	+0.740 (14)	3531
9. <i>m</i> -Chlorobenzoic	-0.37 (5)	-0.280 (12)	3532
10. Acetic	+0.56 (5)	+0.7 (24)	3533
11. <i>p</i> -Chlorobenzoic	-0.22 (5)	-0.104 (12)	3535
12. <i>m</i> -Hydroxybenzoic	-0.12 (5)	-0.219 (12)	3535
13. Benzoic	0.00 (5)	0.00 (24)	3536
14. <i>p</i> -Hydroxybenzoic	+0.34 (5)	+0.270 (12)	3540
15. <i>p</i> -Methoxybenzoic	+0.27 (5)	+0.227 (12)	3541

*Calculated by using the value of Dippy (5) for benzoic acid.

†Calculated from the data of Minnick and Kilpatrick (16).

and intrinsic strengths of some carboxylic acids. The intrinsic strengths are plotted against stretching frequency in Fig. 2. The list is relatively small owing to the lack of experimental data. No suitable data for the calculation of intrinsic strengths of phenols are available at present. Fig. 3 shows the stretching frequencies of the same acids plotted against pK_{r_A} in water. It can be seen that the fit is not materially changed by the fact that intrinsic strengths rather than pK_{r_A} values in water were employed. Thus it appears

that deviations from a single straight line cannot be explained by dielectric effects in the ionizing solvent, and so probably must be ascribed completely to structural factors.

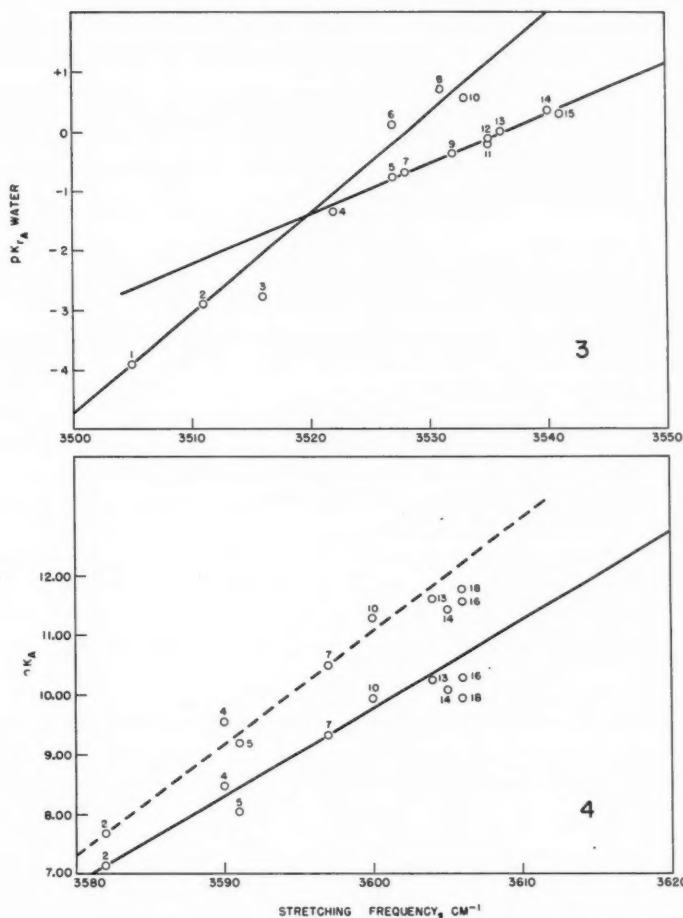


FIG. 3. Plot of O-H stretching frequencies against pK_A in water. (Data from Table II.)

FIG. 4. O-H stretching frequencies of some phenols vs. pK_A in water (solid line) and in 48.9% water-alcohol (broken line). (Data from Table I.)

Fig. 4 shows a plot of stretching frequencies of some phenols vs. pK_A in water (solid line), and pK_A in 48.9% water-alcohol (broken line). The lines are drawn only for visual reference. The effect is to increase the slope of the curve. The compounds toward the bottom of the curve such as nitro and halogeno phenols are affected the least by a change in dielectric. At the other end are the alkyl substituted phenols, which are affected to a much greater extent by variation of dielectric constant of the solvent. It can be seen from equation [1] that such an effect is at least qualitatively in agreement with dielectric theory. The larger the radius of an ion, the smaller the effect of a given change in dielectric would be expected to be. Ions such as *p*-nitrophenolate with large effective

radii due to resonance distribution of the charge are least affected, while the alkyl substituted phenols with resonance of the ion inhibited by such substitution are much more sensitive to variation of dielectric.

The authors obtained much useful data and literature references from an excellent general discussion of dissociation constants and structure by Brown, McDaniel, and Häfliger (4).

ACKNOWLEDGMENT

The authors wish to thank Dr. F. A. L. Anet of this department for the interest and encouragement received in regard to this work.

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THE POLAR EFFECT OF THE β -NITROVINYL GROUP¹

ROSS STEWART AND L. G. WALKER

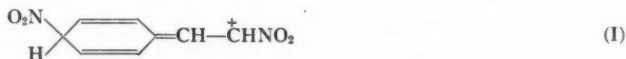
ABSTRACT

The meta and para β -nitrovinyl derivatives of phenol and benzoic acid have been synthesized. The acidity constant, pK_a , was determined for each of these compounds and from these values the following Hammett sigma constants were obtained for the β -nitrovinyl group: $\sigma_{meta} = 0.34$, $\sigma_{para} = 0.26$, $\sigma^- = 0.88$. The relationship between these values and the orienting effect of the β -nitrovinyl group on electrophilic substitution is discussed.

INTRODUCTION

The orienting effect of a substituent in a benzene ring on the position of electrophilic substitution has been satisfactorily rationalized in terms of inductive and resonance effects (6, 17). Most groups which activate electrophilic substitution orient ortho-para and most deactivating groups orient meta. The halogens are the best-known examples of groups which deactivate but orient ortho-para and the postulated independence of resonance and induction satisfactorily accounts for these properties. Vinyl groups which are substituted β by strongly electron-attracting groups are also ring deactivating and strongly ortho-para directing. The β -nitrovinyl group attached to benzene allows less than 2% meta substitution on nitration (1).

One would expect *a priori* the β -nitrovinyl group to be electron withdrawing by both inductive and resonance effects and hence to favor meta substitution. On the other hand the polarizability of an unsaturated side chain might encourage substitution at the ring positions in conjugation, i.e. the ortho and para positions. It has been suggested by Bordwell and Rohde (2) that the following structure helps stabilize the transition state in nitration:



The adjacent positive charges on carbon and nitrogen in the above structure would be expected to raise the energy of this contributing form just as they are believed to do in the case of nitrobenzene (11):



It is still possible, however, that the vinyl group itself can be strongly electron donating by resonance and that the adjacent positive charges do not sufficiently destabilize structure I to prevent it making a significant contribution to the transition state.

A vast body of evidence has accumulated to show that the Hammett equation, $\log k/k_0 = \rho\sigma$, can be used to express the relative rate or equilibrium constant of a reaction of a meta or para substituted benzene derivative in terms of the reaction constant, ρ , and the substituent constant, σ (5). This subject has been reviewed by Jaffé (7). With the exception of certain groups, principally those which conjugate directly with the side chain, it has been shown that a given group has only one σ_{meta} value and one σ_{para} value. Since steric effects are negligible at these positions σ is a measure of the polar effect of group Y on the meta and para positions in the compound C_6H_5Y . It is thus

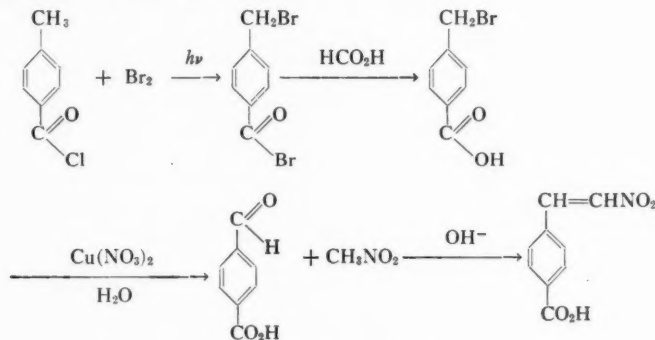
¹Manuscript received June 24, 1957.

Contribution from the Department of Chemistry, University of British Columbia, Vancouver, B.C.

of interest to determine the σ constants for the β -nitrovinyl group in order to correlate, if possible, the polar effect of this group with its known orienting influence.

The ρ values and $\log k_0$ values for the ionization of substituted benzoic acids and phenols are known for various solvents and temperatures and it was decided to determine the constants of the β -nitrovinyl group by measuring the pK_a values for meta and para β -nitrovinylphenol and meta and para β -nitrovinylbenzoic acid.

The synthesis of *p*-(β -nitrovinyl)-benzoic acid is outlined below. A similar sequence produced the meta isomer. The phenols were obtained in one step by condensation of the appropriate hydroxybenzaldehyde with nitromethane. The metasubstituted benzoic acid has not been reported previously.



EXPERIMENTAL

All melting points are uncorrected.

m-(β -Nitrovinyl)-phenol

This compound was prepared through the base catalyzed condensation of *m*-hydroxybenzaldehyde with nitromethane according to the method of Remfry (9), m.p. 136–137°.

p-(β -Nitrovinyl)-phenol

p-Hydroxybenzaldehyde (6.1 g., 0.05 mole) was dissolved in nitromethane (6.1 g., 0.1 mole) and a minimum volume of methanol was added to effect solution. A mixture of methylamine hydrochloride (0.25 g.) and sodium carbonate (0.25 g.) was added and the mixture was heated to boiling for about 1 minute and then cooled in Dry Ice. The crystalline precipitate was recrystallized from ethanol to give 7.1 g. (85%) of pure product, m.p. 165–166°.

ω -Bromo-*p*-toluic Acid

p-Toluoyl chloride was prepared by refluxing *p*-toluic acid (13.6 g.; 0.1 mole) with thionyl chloride (12 ml.) until the free acid dissolved completely. The resulting solution was heated to 160° to remove excess thionyl chloride.

Liquid bromine was added dropwise to the *p*-toluoyl chloride in a beaker at 160° until the uptake of bromine (15.8 g., 0.1 mole) corresponded to 2 gram-atoms per mole of acid chloride. The bromination was done under bright tungsten illumination. The resulting ω -bromo-*p*-toluoyl bromide was hydrolyzed with 85% formic acid (50 ml.) by heating on the steam bath to approximately 40°. The excess formic acid was then allowed to evaporate leaving 21.0 g. of crude ω -bromo-*p*-toluic acid.

Terephthalaldehydic Acid

The crude ω -bromo-*p*-toluic acid (21.0 g.) and 10% aqueous cupric nitrate (300 ml.)

were refluxed for 6 hours. The mixture was allowed to cool, and the solid material collected and crystallized from glacial acetic acid (100 ml.) from which it separated as fine plates. The crude terephthalaldehydic acid was recrystallized from water in the form of very small needles which melted at 248° with decomposition. The phenylhydrazone melted at 221–222°. The yield of pure terephthalaldehydic acid was 5.5 g. (44%).

p-(β -Nitrovinyl)-benzoic Acid

Terephthalaldehydic acid (2.0 g.; 0.02 mole) was condensed with nitromethane by the procedure used for the preparation of *m*-(β -nitrovinyl)-phenol. The resulting product was recrystallized from glacial acetic acid and washed with water, yielding light yellow needles of *p*-(β -nitrovinyl)-benzoic acid (2.2 g., 56%) which melted with decomposition at 283–284°. The reported value is 282° (dec.) (10).

m-(β -Nitrovinyl)-benzoic Acid

This compound was prepared by the same procedure as that used for the para isomer. The yields of ω -bromo-*m*-toluic acid and isophthalaldehydic acid were 63% and quantitative respectively but the condensation of the latter with nitromethane produced *m*-(β -nitrovinyl)-benzoic acid in only 45% yield. Two recrystallizations from water yielded fine light yellow crystals which melted at 193–194°. Calc. for $C_9H_7NO_4$: C, 55.96%; H, 3.65%. Found: C, 55.95%, 56.05%; H, 3.70%, 3.87%.

Ten milligrams of this acid was converted to the acid chloride with thionyl chloride and hence to the methyl ester with methanol. Fine yellow needles of *m*-carbomethoxy- β -nitrostyrene were obtained which after recrystallization from methanol–water melted at 117.5–119°. The reported value is 119° (12).

Determination of Ionization Constants

A typical experiment was conducted as follows. 4-(β -Nitrovinyl)-benzoic acid (0.0081 g.) was dissolved with heating in 70 ml. of distilled water which had previously been boiled to remove dissolved gases. This solution was made up in a 125 ml. conical flask which had four short inlet ports fused around its midsection to accommodate a glass electrode, a calomel electrode, a thermometer, and a nitrogen inlet tube. The whole arrangement was lowered into a constant temperature bath and maintained at 25.0°. Stirring was accomplished by means of an air-driven stirrer which had a Teflon covered bar magnet wired to the chuck. This was placed immediately below the titration flask in the bath and worked quite satisfactorily under water. Another Teflon-covered bar magnet was placed in the titration flask. Stirring was controlled by regulating the air pressure. A microburette containing 0.025 *N* carbonate-free potassium hydroxide was fixed in position above the titration flask so that the burette tip intruded into the flask. This and other openings to the flask were loosely sealed with Tygon gaskets. A slow stream of carbon dioxide free nitrogen was run through the system during the experiment. The acid was titrated with the standard base and when pH readings were made both air and bath stirrers were shut off. The pH was measured with a Beckman pH meter, model G, standardized before and after titration against buffer at pH 7.00. The precision of the pH readings was 0.01 pH unit.

Calculation of pK_a

The pH was plotted against volume of base added and in all cases except that of *m*-(β -nitrovinyl)-phenol typical titration curves were obtained with a clearly distinguishable equivalence point, which was taken as the point of maximum rate of pH change. In all cases this point agreed satisfactorily with that calculated from the weight of material used. In the case of the metasubstituted phenol the acid is so much weaker that the

equivalence point had to be calculated from the weight of material used.

The pK_a values were obtained from the following equation (4):

$$[H^+] = K_a([HA]_0 - [A^-] - [H^+] + [OH^-]) / ([A^-] + [H^+] - [OH^-]).$$

This can be converted to the following expressions for solutions above and below pH 7:

$$pK_a = pH - \log\{([A^-] + [H^+]) / ([HA] - H^+)\} \quad \text{if } pH < 7,$$

$$pK_a = pH + \log\{([HA] + [OH^-]) / ([A^-] - [OH^-])\} \quad \text{if } pH > 7.$$

In these equations $[HA]_0$ stands for the original concentration of acid and $[HA]$ and $[A^-]$ stand for the concentrations of acid and salt present at any stage of the titration calculated from $[HA]_0$ and the amount of base added.

The pH values corresponding to 40, 50, and 60% titration were used to calculate pK_a and in most cases gave identical values for pK_a .

Table I lists the pH at half titration and the pK_a obtained from it and the above equations for the β -nitrovinyl-substituted benzoic acids and phenols. In addition values for benzoic acid and *m*-chlorobenzoic acid are listed as a check.

TABLE I
ACIDITY CONSTANTS OF BENZOIC ACIDS AND PHENOLS IN WATER AT 25°

Acid	Molarity, $\times 10^{-4}$	pH at half titration	pK_a
Benzoic	6	4.34	4.21 ^a
	12	4.29	4.21
<i>m</i> -(β -Nitrovinyl)-benzoic	6	4.12	3.90
	12	4.02	3.87
	20	3.95	3.86
<i>p</i> -(β -Nitrovinyl)-benzoic	6	4.15	3.94
	6	4.15	3.94
<i>m</i> -Chlorobenzoic	6	4.07	3.82 ^b
<i>m</i> -(β -Nitrovinyl)-phenol	6	9.09	9.12
	12	9.04	9.08
<i>p</i> -(β -Nitrovinyl)-phenol	6	7.98	7.98
	12	7.98	7.98

^aJaffé lists 4.203 as the mean value of pK_a for benzoic acid (7).

^bUsing the accepted value of 0.373 for the σ constant for *m*-Cl (7) the pK_a of *m*-chlorobenzoic acid should be 3.830.

Ultraviolet Spectra

The spectra of the nitrovinyl compounds were obtained in aqueous solution using a Cary recording spectrophotometer, model 14. Since the spectrum of *p*-(β -nitrovinyl)-phenol is markedly different from that of its anion (Fig. 1) the acidity constant of this acid was determined spectrophotometrically as a check on the titration method. The pH of a 3.5×10^{-5} *M* solution of the substance was brought approximately to the pK_a value using a 10^{-3} *M* borate buffer, and the spectrum of the solution determined. Using the optical densities at 456 and 363 $m\mu$ the concentration of the two species, the phenol and its anion, can be obtained. Correction was made for the small absorption by the anion at 363 $m\mu$. The pH of the solution was then measured with the glass electrode. A similar attempt using *m*-(β -nitrovinyl)-phenol was less successful since the spectrum of the anion differs only slightly from that of the phenol. The tail which extends into the visible was used, the absorption at 440 $m\mu$ representing the concentration of anion, but the precision of the results is not great. The results of the spectrophotometric determination of acidity constants are shown in Table II.

TABLE II
 ACIDITY CONSTANTS OF THE β -NITROVINYLPHENOLS FROM THEIR ULTRAVIOLET SPECTRA

Phenol	$M, \times 10^{-5}$	D_{456}	D_{363}	pH	pK_a
<i>p</i> -(β -Nitrovinyl)	3.5	0	0.57	3.8	—
	3.5	0.76	0.12	10.4	—
	3.5	0.31	0.40	7.80	7.99
	3.5	0.49	0.29	8.19	7.98
<i>m</i> -(β -Nitrovinyl)	8.75	0	0.85	3.3	—
	8.75	0.13	0.83	10.5	—
	17.5	0.15	1.62	9.16	9.02
	17.5	0.14	1.62	9.07	8.99

It can be seen that the agreement between the values in Tables I and II is excellent for *p*-(β -nitrovinyl)-phenol but is less satisfactory for the meta isomer. This is not unexpected in view of the small difference between the spectrum of the phenol and the ion and in view of the fact that the equivalence point of the titration has to be estimated from the quantity of material used. An additional difficulty is the fact that β -nitrostyrenes are decomposed slowly by hydroxyl ion (13).

DISCUSSION

The nitrovinyl compounds studied in this work have a very low water solubility and it initially seemed preferable to determine their acidities in aqueous alcohol solution. However, erratic results were obtained for the pK_a values of the phenols, in particular, *p*-(β -nitrovinyl)-phenol for which different values of σ were obtained depending on the composition of the solvent. This phenomenon might have been expected since in the *p*-(β -nitrovinyl)-phenolate ion a considerable fraction of the change resides on the substituent group. Thus, changes in the medium would be expected to affect the solvation not merely at the reaction site but at the substituent as well and hence affect the entropy. In this connection Jaffé (7) has pointed out that σ values need not be completely independent of solvent as has often been assumed. An additional difficulty in using mixed solvents with the glass electrode is the problem of evaluating the correction (see Experimental section) required to convert the pH at half titration to the pK_a since even in 50% ethanol the compounds are not very soluble.

Accordingly, it was decided to use water as the solvent despite the low solubility of the compounds. The accuracy of the method used is high as shown by the determination of pK_a for benzoic acid and *m*-chlorobenzoic acid shown in Table I. The σ values were calculated using the Hammett equation and the values 4.20 and 9.85 for $\log k_0$ for benzoic acid and phenol, respectively, and the values 1.000 and 2.113 for ρ . The results for both the titration method and the spectrophotometric method are shown in Table III.

The value of σ_{meta} should be the same for both the substituted benzoic acid and the phenol and the agreement is satisfactory in view of the inaccuracies present in the determination of pK_a for the phenol. A mean value of 0.34 is suggested for σ_{meta} for this group. The large value of σ_{para} for the β -nitrovinyl group in phenol is to be expected since direct resonance interaction can occur between the substituent group and the reacting center. The β -nitrovinyl group thus should be classed with those groups, notably nitro, which have dual sigma constants for the para position. Taft (14) uses the symbol σ^- for the constant used with derivatives of phenol and aniline. Table IV compares σ_{para} and σ^- for the β -nitrovinyl group and some of the other groups which have dual constants.

TABLE III
 σ VALUES FOR THE β -NITROVINYL GROUP

Compound substituted	Position	σ	Mean value
Benzoic acid	<i>p</i>	0.26	0.26
		0.26	
Benzoic acid	<i>m</i>	0.30	0.32
		0.33	
		0.34	
Phenol	<i>p</i>	0.884	0.883 ^a
		0.884	
		0.879 ^b	
		0.884 ^b	
Phenol	<i>m</i>	0.36	0.37
		0.34	
		0.39 ^b	
		0.40 ^b	

^aThe precision of the results for this compound warrants the inclusion of the third significant figure.

^bSpectrophotometric determination.

It is worth mentioning that because of this strong resonance interaction the β -nitrovinyl group should activate nucleophilic substitution at the para position, the same position that is preferentially attacked by electrophilic reagents.

Comparison of σ_{para} and σ_{meta} shows that like the halogens the β -nitrovinyl group has a larger sigma value in the meta than the para position. The positive sign for these values shows that the group is electron withdrawing in agreement with its deactivating influence on electrophilic substitution. The larger value in the meta position is in agreement with its ortho-para directing influence (16). (Brown and Okamoto (3) have recently published values for σ^+ , a Hammett-type function for use with aromatic substitution reactions. In no case is the relative order of σ^+_{meta} and σ^+_{para} different from that of σ_{meta} and σ_{para} .) Indeed, the sigma values are very close to those for the iodine atom, i.e. $\sigma_{\text{meta}} = 0.35$ and $\sigma_{\text{para}} = 0.28$ for iodine compared to $\sigma_{\text{meta}} = 0.34$ and $\sigma_{\text{para}} = 0.26$ for β -nitrovinyl. Taft (15) has recently attempted to split σ_{para} into two components, σ_I and σ_R , representing the inductive and resonance interaction between the substituent and the benzene ring. This conversion requires a knowledge of the rates of reaction of aliphatic derivatives of the group in question, information which is apparently not available for the β -nitrovinyl group. However, in view of Taft's results σ_I and σ_R are probably not greatly different for $-I$ and $-CH=CHNO_2$. The values for iodine are $\sigma_I = +0.38$ and $\sigma_R = -0.10$.* One can infer from this that the nitrovinyl group is deactivating by induction and ortho-para directing by resonance. From this one would predict that the unsubstituted vinyl group will be found to have a larger negative value of σ_R , i.e. be strongly electron donating by resonance.

Dr. Taft in a personal communication has kindly pointed out that σ_I and σ_R can be calculated for the β -nitrovinyl group as follows. For the group $CH_3CH=CHCH_2-$, $\sigma^ = +0.13$ (15). Therefore, $\sigma_I = \sigma' = 0.45 (+0.13) = +0.06$ for the $CH_3CH=CH-$ group (15). Now $\sigma_{\text{I}}^{\text{NO}_2} - \sigma_{\text{CH}_3}^{\text{CH}_3} = +0.63 - (-0.05) = +0.68$ and if the additive rule applies then σ_I for the $O_2NCH=CH-$ group should be $0.06 + 0.68/X$, where X is the reduction factor for the $C=C$ system. The ratio of the ρ values for the ionization of cinnamic and benzoic acids, $1.000/0.466 = 2.1$, apparently gives an appropriate value of X . Thus, σ_I for the β -nitrovinyl group should be $+0.38$. This may be checked independently using the data reported herein and the following equations (14, 15):

$$\begin{aligned}\sigma_{\text{para}} &= \sigma_I + \sigma_R \\ \sigma_{\text{meta}} &= \sigma_I + \frac{1}{3}\sigma_R\end{aligned}$$

This gives $\sigma_I = 3(\sigma_{\text{meta}}) - (\sigma_{\text{para}}) = (3(0.34) - 0.26)/2 = +0.38$ in exact agreement with the above value. Thus $\sigma_R = \sigma_{\text{para}} - \sigma_I = 0.26 - 0.38 = -0.12$ and both σ_I and σ_R for β -nitrovinyl are very close to those for iodine as concluded above.

TABLE IV
COMPARISON OF σ_{para} AND σ^- FOR GROUPS WITH DUAL
CONSTANTS^a

Group	σ_{para}	σ^-
$-\text{CH}=\text{CHNO}_2$	0.26	0.88
$-\text{NO}_2$	0.78	1.27
$-\text{C}\equiv\text{N}$	0.63	1.00
$-\text{CHO}$	0.22	1.13
$-\text{COCH}_3$	0.52	0.87

^a Taken from Jaffé (7) with the exception of the values for β -nitrovinyl.

Ultraviolet Spectra

Since much of the previous discussion is concerned with ionic structures an examination of the ultraviolet spectra of the various compounds studied in both acidic and basic solution is of interest. Figs. 1-4 show these spectra and Table V lists values of λ_{max} and molecular extinction coefficient.

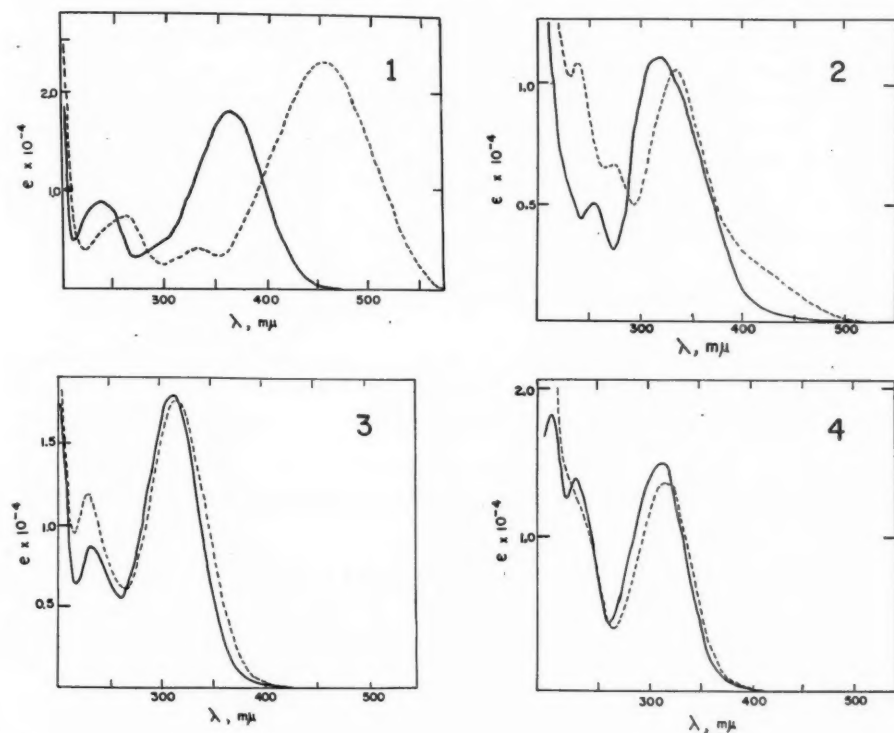


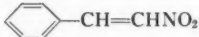
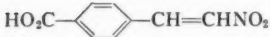
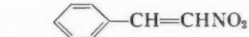
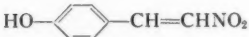
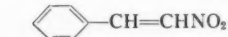
FIG. 1. Ultraviolet spectra of *p*-(β -nitrovinyl)-phenol (solid line) and its anion (broken line).

FIG. 2. Ultraviolet spectra of *m*-(β -nitrovinyl)-phenol (solid line) and its anion (broken line).

FIG. 3. Ultraviolet spectra of *p*-(β -nitrovinyl)-benzoic acid (solid line) and its anion (broken line).

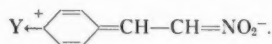
FIG. 4. Ultraviolet spectra of *m*-(β -nitrovinyl)-benzoic acid (solid line) and its anion (broken line).

TABLE V
 ULTRAVIOLET ABSORPTION MAXIMA FOR β -NITROVINYL COMPOUNDS IN WATER SOLUTION^a

Compound	Acid form		Anion	
	λ_{\max} , m μ	$\epsilon \times 10^{-4}$	λ_{\max} , m μ	$\epsilon \times 10^{-4}$
 <chem>C=CC1=CC=C(C=C1)[N+](=O)[O-]</chem>	320	1.33	—	—
 <chem>C=CC1=CC=C(C=C1C(=O)O)[N+](=O)[O-]</chem>	313	1.80	319	1.72
 <chem>C=CC1=CC=C(C=C1C(=O)O)[N+](=O)C1=CC=CC=C1</chem>	316	1.39	318	1.34
 <chem>C=CC1=CC=C(C=C1)[N+](=O)[O-]</chem>	363	1.78	456	2.32
 <chem>C=CC1=CC=C(C=C1)[N+](=O)[O-]</chem>	318	1.13	331	1.02

^aThe solutions contained 0.5% ethanol.

The only compound which shows a bathochromic shift in the un-ionized form compared to β -nitrostyrene is *p*-(β -nitrovinyl)-phenol, which is expected to because of the direct resonance interaction referred to earlier and which again, as expected, is much larger in the anion. The anion of *m*-(β -nitrovinyl)-phenol also had its absorption shifted to longer wavelengths, presumably by a secondary resonance effect (8). Kamlet and Glover (8) examined the spectra of some parasubstituted β -nitrostyrenes and have shown that electron withdrawing groups cause a hypsochromic shift presumably because of an increase in energy of such structures for the excited state as



The decrease in λ_{\max} shown in Table V when a carboxyl group is substituted para and the subsequent increase when this group is converted to the anion by base is in agreement with this picture.

ACKNOWLEDGMENT

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NOTES

THE SYNTHESIS OF 3-INDOLEACETIC ACID-C¹⁴ LABELED IN THE BENZENE RING¹

J. R. ROBINSON

3-Indoleacetic acid (IAA) is a plant metabolite which regulates the growth and differentiation of plant tissues. Because of the extremely small amounts of endogenous IAA associated with growth effects, material labeled with carbon-14 is of value in attempts to elucidate the metabolic fate of the hormone.

Labeled 3-indoleacetic acid has been synthesized previously with the active carbon atom in the carboxyl (7) and alpha (2, 6, 9) positions of the side chain, as well as in the 2-position of the pyrrole ring (5). All these materials have a common disadvantage: in the plant, the radioactive marker atom is readily lost as carbon dioxide and it becomes impossible to trace the later stages of degradation. This report describes a convenient method of synthesis for indoleacetic acid-C¹⁴ labeled in the benzene ring where the marker atom is likely to be more stable and thus provide radioactive degradation products. The material has been made with the ring labeled generally, as well as specifically in the 7-*a* position. The synthesis of the latter compound is described in detail.

EXPERIMENTAL

Labeled aniline-1-C¹⁴ hydrochloride (76 mg., 500 μ c.) was added to 121 mg. of inactive aniline hydrochloride in a 100 ml. (24/40) round-bottomed flask, making a total of 1.52 mM. of the salt. This was dissolved in 2 ml. of 1 *M* HCl and diluted to 15 ml. with water, chilled to 0° C., and treated, dropwise with cooling, with 1.8 ml. of 1 *M* sodium nitrite. The cold diazonium salt solution was immediately treated with a freshly prepared solution of sodium bisulphite (prepared by saturating, with sulphur dioxide, a cooled solution of 981 mg. (24.4 mM.) of sodium hydroxide in 15 ml. of water (1)) and warmed on the steam bath, under a watchglass, for 5 hours. The cover was then removed, 5 ml. of conc. HCl was added dropwise, and heating was continued overnight, with a jet of dry nitrogen directed upon the surface of the solution to remove the water and dissolved gases.

The dry, white, crystalline mixture of phenylhydrazine hydrochloride and sodium chloride was suspended in 20 ml. of conc. HCl containing 5 ml. of 85% phosphoric acid. With swirling and cooling, a solution of 2-ketoglutaric acid (236 mg., 1.6 mM.) in 15 ml. of pyridine² was added, dropwise. The mixture was then heated under reflux for 2 hours, cooled, and diluted with water to 100 ml.

The diluted acidic reaction mixture was extracted for 11 hours with 100 ml. of ether in a suitable continuous extraction apparatus (4). The ether extract was washed with two 15-ml. portions of 1% potassium hydroxide and the pH of the combined aqueous phases was adjusted to the point of cloudiness by adding 85% H₃PO₄ dropwise, with stirring. The solution was then just cleared by the addition of a few drops of 5% KOH. (The pH at this point is 4.5-5.) The acid solution was diluted to 100 ml. and again extracted with 100 ml. of ether, as above, for 5 hours. The ether extract was concentrated, under a stream of dry nitrogen, to a tan-colored oil and transferred, with ether

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²For the use of a pyridine-HCl mixture in the decarboxylation of certain steroid acids see Ref. 3.

washings, to a semimicro vacuum sublimation apparatus (8). On removal of the ether, the crude product crystallized. The cold-finger was inserted and the system was evacuated thoroughly with a water aspirator (15 mm.) for 30 minutes. A higher vacuum (0.2 mm.) was then applied and the product was sublimed using a mineral oil bath at 80–100° for 5 hours. The sublimation was interrupted and the first crop of labeled 3-indoleacetic acid was washed from the cold-finger with absolute ethanol. The unsublimed residue was treated with 2 ml. of ether and the solvent evaporated, with swirling, to present a fresh surface of the crude material. The sublimation was then resumed for a further 5 hours, and the process repeated. Operating in this way, three crops of 3-indoleacetic acid-7a-C¹⁴ were collected, total weight 184 mg. (69% from aniline), m.p. 169–170°.

Using an end-window counter (2 mg./cm.² thickness) and standard counting techniques, the material had an activity of about 4×10^5 counts per minute per milligram. Paper chromatography, followed by autoradiography, showed the material to be of high radiochemical purity.

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ISOPIESTIC TECHNIQUES APPLIED TO PHASE DIAGRAM DETERMINATION IN THE SYSTEMS SILVER-CADMIUM AND COPPER-CADMIUM¹

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Phase relationships in alloys have, in certain cases, been deduced from changes of thermodynamic activity with composition—see, for example, Strickler and Seltz (9). Such measurements are, in general, experimentally more difficult than standard phase diagram work. The two methods described here, however, are comparatively simple and require no elaborate apparatus. The modern form of the isopiestic technique for comparing activities of non-metallic solutions is due to Sinclair (8). Scatchard (7) has used this technique to determine solubilities in aqueous solution, but it has seldom been applied to metal systems, either for phase-boundary determinations, or for calculation of activities by comparison with a system of known activity.

The first of the methods to be described here, which is dependent upon the establishment of neutral equilibrium, was not completely reliable in the present case. Results obtained by the second method are in close agreement with those of earlier investigations. Both methods are applicable to binary systems in which the volatility of one component

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is negligible compared with the other. Knowledge of the actual vapor pressures, or activities, of the alloys is not required, the operating principle being the constancy of vapor pressure over any two-phase region. The systems copper-cadmium and silver-cadmium were chosen to test the methods, since most of the phase-boundaries in these systems appeared to have been accurately located by more conventional means.

First Method

Solubilities, particularly in gas-metal systems, can be measured by exposing metals to controlled atmospheres containing the solute gas at the dissociation pressure of the saturated solid solution. A simpler technique, in which the gas pressure is controlled by using the nearest compound in the equilibrium diagram as the gas source, has been described by Caplan *et al.* (1) and is similar in principle to the present method.

Filings were prepared from 99.999% pure copper, magnetically separated from iron particles introduced in filing, degreased, and dried. A two-phase alloy ($\alpha + \beta$) was made by absorption of 99.99% pure cadmium from the vapor, to give about 0.3 g. of alloy, which was then sealed in vapor contact with carefully weighed filings of the pure copper. The specimen tubes were placed side by side, to minimize temperature differences, in a furnace at 500° C. The temperature was controlled to within 1.5° C. of this value. Composition changes were followed by cooling the specimens in an air blast after successive intervals of time, and weighing them. Very rapid quenching of the pyrex container relative to the specimens was avoided; otherwise there would have been excessive loss of cadmium to the walls of the container.

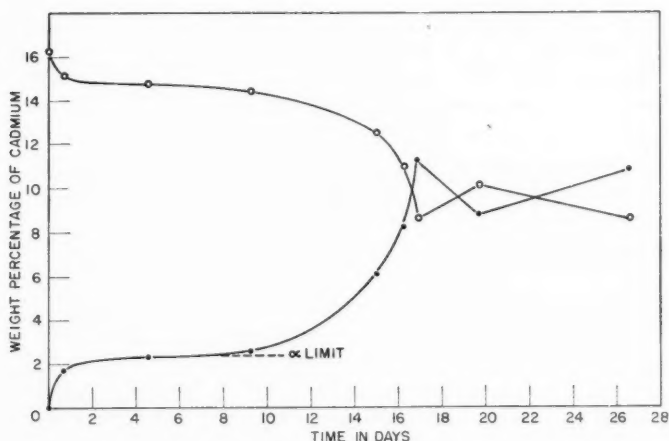


FIG. 1. Attainment of "neutral equilibrium" between Cu-Cd alloys. ● originally pure Cu; ○ alloys contain two phases ($\alpha + \beta$), and supply a constant vapor pressure of Cd.

It is seen in Fig. 1 that the approach to the α solubility limit was asymptotic; the "horizontal" portion of the lower curve, which occurs between 2.3 and 2.5 weight per cent cadmium, is in agreement with the solubility of 2.4% given by Raub (6), and close to that of Jenkins and Hanson (3), namely 2.7%. Although there should have been no driving force for further reaction at this stage, the solubility limit was, nevertheless, eventually exceeded, presumably owing either to precipitation of the β phase from

saturated α on cooling, or to temperature differences between the specimens, of such magnitude as to be almost unavoidable in the average furnace. Even so, the true solubility could be estimated from the first part of the curve. The repeated crossings of the curves in later stages are attributed to one specimen being alternately slightly hotter and colder than the other, after replacement in the furnace. These shifts in composition are far in excess of weighing errors, which were about 0.05%.

Second Method

Pairs of isopiestic binary solutions of cadmium in silver and copper were prepared. Phase-boundaries were then located simultaneously for both systems, by plotting the equilibrium percentages of cadmium in silver against the corresponding compositions of the copper alloys as in Fig. 2.

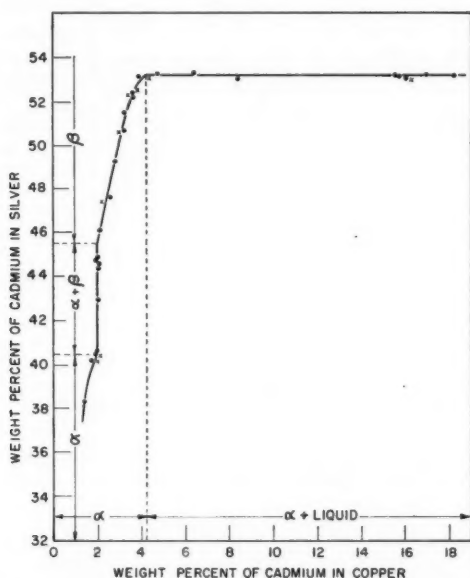


FIG. 2. Isopiestic compositions in the systems Ag-Cd and Cu-Cd. ● weighed; × chemical analysis.

The alloys were made by absorbing cadmium vapor in fine filings of the competing solvents. The silver was purified by electrolysis to give a composition of 99.999%. The copper and cadmium were the same grades as used in the first method. Approximately 0.5 g. samples of the three metals were weighed in individual Vycor tubes, which were then sealed in an evacuated pyrex envelope and annealed at 610° C., the highest temperature the pyrex could withstand for some days without collapsing. During the approach to equilibrium, compositions were checked by weighing. The attainment of equilibrium was shown by a distinct change in direction, where the non-equilibrium points merged with the true isopiestic line. The final compositions in critical regions were verified by chemical analysis. After equilibrium had been established, successive points still moved slowly, owing to loss of the cadmium vapor in the tube, at the time of quenching. The various branches of the equilibrium curve, together with the phase-fields they represent,

are shown in Fig. 2. Two-phase regions of the copper system are represented by horizontal and those of the silver system by vertical lines. In the single-phase regions, the isopiestic line curves towards the axis representing the system with the greater activity coefficient, γ (defined as activity divided by atomic concentration, c , of solute). This is generally true. For any system, $d^2\gamma/dc^2$ will tend to be the more negative, the higher the values of γ for that system, since all γ versus c curves must approach unity at high concentrations of solvent. This discussion applies more properly to diagrams plotted in atomic per cent. The curvatures of the single-phase regions of Fig. 2 are changed very little, however, if plotted in atomic, instead of weight, per cent.

The experimental phase-boundaries are close to those determined by previous investigators. Raub's value (6) of 4.35 wt.% for the solubility of cadmium in copper is slightly greater than the present value of 4.2%. The 40.5% solubility of cadmium in silver agrees exactly with the results of Hume-Rothery *et al.* (2) and is close to the 40.6% estimated from the data of Owen and Roberts (4). The silver-cadmium ($\alpha + \beta$)/ β boundary is placed at 45.5% Cd, i.e. 0.7% lower than the position given by Owen, Rogers, and Guthrie (5), who had difficulty in retaining the β phase on quenching. For this reason, the present evaluation may be preferred, since decomposition on quenching does not affect the results.

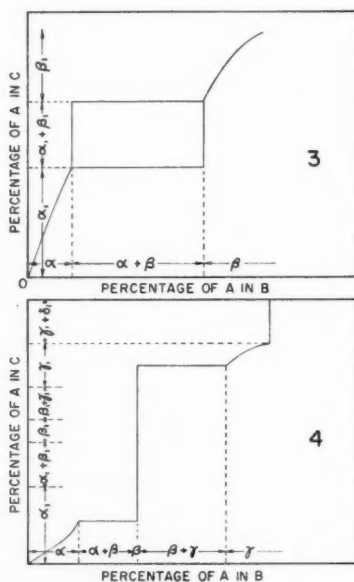


FIG. 3. The rectangle encloses an isopiestic region, the vapor pressures of the two-phase alloys in both systems being identical.

FIG. 4. The large change of vapor pressure on traversing the invariant β phase prevents observation of four phase-boundaries in AC .

Possible complications, although not encountered in the above experiments, should perhaps be mentioned, for example: (a) The terminal solid solutions of both systems could conceivably be followed by two-phase fields of identical vapor pressure. All points within the rectangle of Fig. 3 would be experimentally possible. This situation is unlikely to

arise, but could be recognized by approaching equilibrium from opposite directions. (b) A compound, β , of invariant composition, in a system AB , could be confused with a two-phase region of the system AC on a plot of the type represented in Fig. 4, since both would appear as vertical lines. This ambiguity disappears when neighboring branches of the isopiestic curve are considered. (c) The change of activity on traversing the unique composition of an invariant compound may be great enough to include the activity levels of various two-phase fields of the other alloy systems, as in Fig. 4, in which case the boundaries of these regions would remain unnoticed. Such difficulties may be overcome by establishing equilibrium between an unknown and a known system, the latter preferably consisting of either a continuous range of solid solution, or of wide terminal solutions with no intermediate compounds.

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A CORRELATION OF ELECTRIC DIPOLE MOMENTS OF SUBSTITUTED BENZENES BY REACTIVITIES¹

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The resultant dipole moment of a molecule has been considered to be the vector sum of the individual bond or group moments. But in many cases, in particular the benzene derivatives, the observed dipole moment differs markedly from the values calculated from group moments and this has been explained as due to resonance contribution. Resonance seems to account for the influence of the substituents on dipole moments just as on the reactivity of organic compounds. The electron density at the reaction center is determined by the electron withdrawing or donating power of the substituents. The reactivities or the substituent constants derived by Hammett (2), Brown (1), and others are a measure of the ability of the substituents to change the electron density at the reaction center. The substituent constant is negative or positive depending on whether the substituent is electron contributing or withdrawing. The greater the effect of the substituent on the electron density, the larger the numerical value of the substituent constant. Brown σ^+ -values differ from the Hammett σ -values by a resonance term resulting from the greater opportunity for resonance contributions by the substituent in electrophilic reactions (4). One would therefore predict a relation of the dipole

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moments of substituted benzenes with reactivities. However, such a correlation would only be a crude approximation and the substituents for which the observed dipoles are rough measures of the charge distribution can be expected to follow this correlation. Further, it should be noted that in some cases the values of the substituent constants themselves have large uncertainties. The object of this communication is to present a correlation (however crude it may be) of electric dipole moments of substituted benzenes with the substituent constants, and we have not discussed the details of the correlations or explained the deviations. All the dipole moment values were selected from the literature (8) and are measurements made in benzene solution at or around 25° C.

Figure 1 shows a plot of the dipole moments (μ) of monosubstituted benzenes against the Hammett σ_{para} values (3). There seems to be an approximately linear relationship

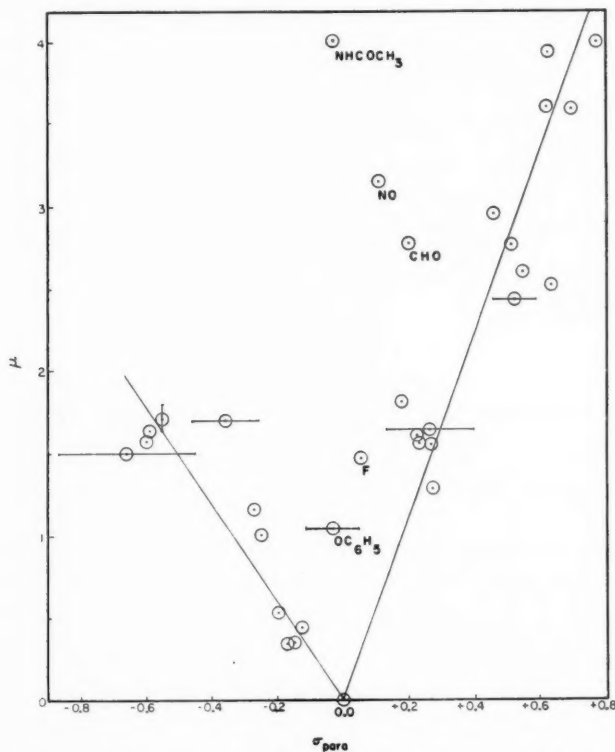


FIG. 1. Correlation of dipole moments of monosubstituted benzenes with the substituent constants.

following the equation

$$[1] \quad \mu = \rho\sigma,$$

where ρ is the slope of the line. A similar relationship is also observed when the σ_{para}^+ values are used as the substituent constants. As can be expected, groups like F, OC_6H_5 , NHCOCH_3 , and NO show wide deviations from the correlation [1]. Since μ of benzene itself is zero, two straight line plots are obtained, one with a negative slope (electron

donating groups) and another with a positive slope (electron withdrawing groups). The slopes of the two lines shown in Fig. 1 are about 5.5 and -3.0 .

When the dipole moments of a series of para- and meta-disubstituted benzenes (substituents R_1 and R_2 , where R_1 is kept invariant in a series) are plotted against the Hammett σ -values of the varying substituents R_2 , an approximately linear relationship is noticed only when the two substituents have opposing electrical properties (ortho-para versus meta-orienting). This correlation was found to hold for all the series of di-substituted benzenes tried. In Fig. 2 are shown plots of μ versus σ for a few series of

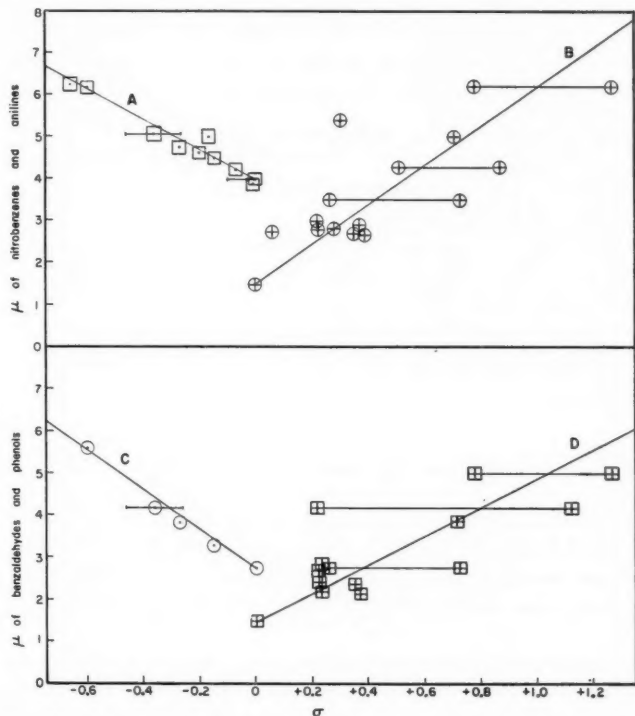


FIG. 2. Correlation of dipole moments of *m*- and *p*-disubstituted benzenes with the substituent constants. A, monosubstituted nitrobenzenes; B, monosubstituted anilines; C, monosubstituted benzaldehydes; D, monosubstituted phenols.

disubstituted benzenes. This relationship can be expressed as

$$[2] \quad \mu = \rho' \sigma + C,$$

where ρ' is the slope of the line and C , the intercept on the ordinate at $\sigma = 0$. The use of σ^+ -values also shows a similar proportionality. No such simple relationship is apparent when the two substituents possess like electrical properties. In general, complimentary disubstitution results in larger dipole moments and the greater the contrast in electrical properties of the groups, the larger the value of the dipole moment. In the case of the monosubstituted nitrobenzenes, the relation [2] seems to hold good even when the varying substituents are electron withdrawing groups. In Fig. 2, for groups like NO_2 and COOH ,

Hammett σ -values are shown as the lower limit and the "dual" σ -values (3) as the upper limit. A value in between these two limits would seem to correlate the μ values for these groups.

There appears to be no simple relation of dipole moments of disubstituted benzenes with Taft's resonance and inductive parameters (7). The limited amount of data available do not permit any definite conclusions to be drawn. Similar correlations of the ultraviolet absorption spectra of substituted benzenes with reactivities have been made (5). However, the use of Taft's resonance parameters seems to be of greater significance here (6).

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SYNTHESIS OF INDOLEACETIC ACIDS¹

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In cold-run studies leading to a semimicro synthesis of 3-indoleacetic acid-C¹⁴ labeled in the benzene ring, the reaction sequence illustrated on the following page was investigated.

The method closely parallels that of Feofilaktov and Semenova (1, 2). Unfortunately, owing to the rather limited abstract information available to us, we were unable to confirm the excellent yields reported by the Russian workers. Only with several modifications were we able to obtain 3-indoleacetic acid in an over-all yield of 40% from aniline. These modifications, listed below, may be of general interest in the field of indole-acid synthesis.

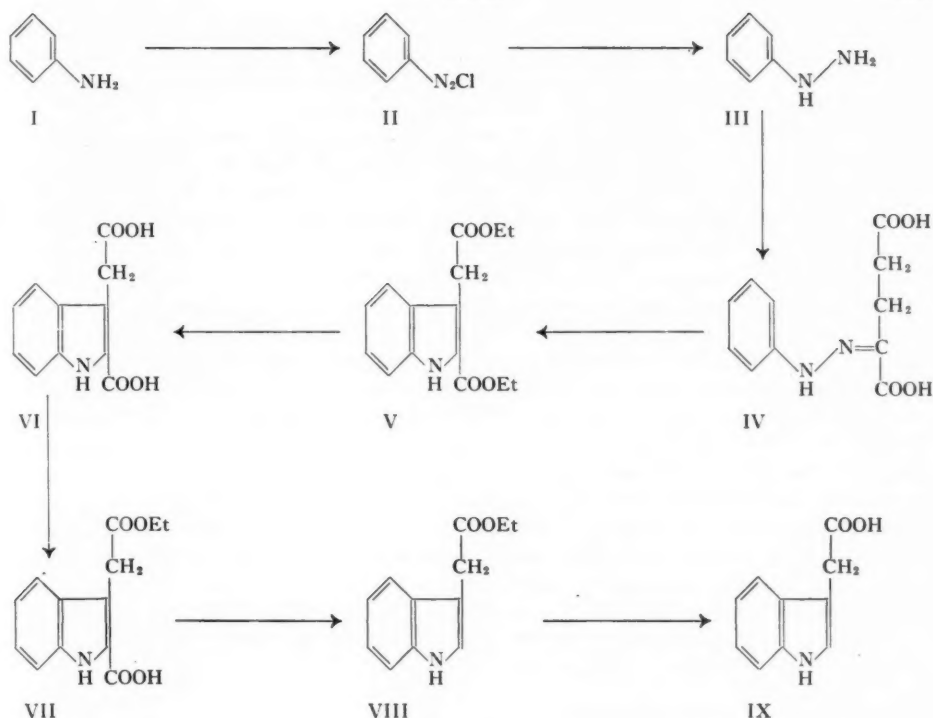
The cyclization medium (absolute ethanol saturated with hydrogen chloride) was modified to include about 5%, by weight, of polyphosphoric acid. This raised the boiling point and ensured an anhydrous medium.

The phenylhydrazone of 2-ketoglutaric acid (IV) (2, 3, 5) was substituted for that of ethyl 2-keto-4-cyanobutyrate (1, 4, 6), eliminating several transfers.

The half-ester (VII), of a type reported by King and L'Ecuyer (5), was found to be more amenable to decarboxylation than was the diacid (VI).

The use of red cuprous oxide instead of copper powder, with quinoline, effected a much smoother decarboxylation at a lower temperature.

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To aid in the extraction of the decarboxylated product (VIII) from the tarry residues, only 1 to 2 equivalents of quinoline was used, and the bulk of the decarboxylation medium consisted of diethylene glycol. This allowed the reaction mixture to be "quenched" in dilute HCl and extracted with ether, eliminating the necessity of a high vacuum distillation.

EXPERIMENTAL

Phenylhydrazine (III)

Using a weighed, 250 ml. (24/40) round-bottomed flask, 650 mg. (5 mM.) of aniline hydrochloride was dissolved in 15 ml. of 1 *M* HCl and diluted to 25 ml. with water. Diazotization was accomplished at 0° C. using 5 ml. of 1 *M* sodium nitrite. The cold diazonium salt solution was immediately treated with a freshly prepared solution of sodium bisulphite (prepared by saturating, with sulphur dioxide, a cooled solution of 960 mg. (24 mM.) of sodium hydroxide in 15 ml. of water) and warmed on the steam bath, under a watchglass, for 5 hours. Five milliliters of conc. HCl was then added dropwise and heating continued overnight, with a jet of dry nitrogen directed upon the surface of the solution to remove the water and dissolved gases.

2-Carboxy-3-indoleacetic Acid (VI)

The dry mixture of phenylhydrazine hydrochloride and sodium chloride was dissolved in 10 ml. of water and treated with 730 mg. (5 mM.) of 2-ketoglutaric acid dissolved in 5 ml. of water. The resulting clear solution was chilled in ice water with the formation of a

yellow oil which crystallized when it was left standing overnight. The mother liquors were removed using a vacuum and "filter-stick" and, after being washed once with water, the yellow solid (IV) was dried *in vacuo* over calcium chloride. Weight, 1019 mg.; m.p. 158–159° with decomposition; yield 86% from aniline.

The cyclization medium consisted of 100 ml. of commercial "absolute" ethanol containing 5 g. of polyphosphoric acid and saturated, in the cold, with dry hydrogen chloride. This solution was poured on the dried phenylhydrazone, warmed to the boiling point, and again treated with HCl. The strongly acid solution was then heated under reflux for 3½ hours, with moisture excluded. The reflux condenser was then replaced by a still head and most of the ethanol was distilled away from the mixture. The residue, 20–30 ml., containing much precipitated ammonium chloride, was washed with stirring into 200 ml. of a crushed ice and water mixture and left standing overnight in the refrigerator. The resulting diester (V) was isolated by removal of the mother liquors with a filter-stick. After one washing with water the product was transferred, by means of a syringe pipette, with 25 ml. of 95% ethanol to a 60 ml. (19/22) round-bottomed flask. Potassium hydroxide (500 mg.) was added and the solution was warmed on the steam bath under a jet of nitrogen, keeping the volume constant by regular additions of water. When the alcohol was mostly replaced with water (3 hours), the flask was immersed in a boiling water bath and the evaporation continued for another hour. The aqueous solution was then cooled and, slowly with swirling, was acidified with phosphoric acid to pH 2. On standing overnight in the cold, the 2-carboxy-3-indoleacetic acid (VI) crystallized. The supernatant was removed with a filter-stick and the product washed once with cold water. It was dried thoroughly *in vacuo* over calcium chloride and weighed 700 mg. (64%, from aniline), and melted with decomposition at 235–236°.

Ethyl 2-Carboxy-3-indoleacetate (VII)

One milliliter of commercial "absolute" ethanol was cooled and saturated with dry hydrogen chloride. The solution was then diluted to 10 ml. with ethanol and poured on the dried diacid. The flask was stoppered and left at room temperature for 1 hour.

Two milliliters of concentrated ammonium hydroxide was diluted with water to 45 ml. This solution, cooled, was added all at once to the acidic, alcoholic solution of half-ester. The resulting clear, weakly alkaline solution was chilled in ice water and, while swirling, sufficient phosphoric acid was added dropwise to precipitate the half-ester at pH 2. After crystallization was complete the mother liquors were removed with a filter-stick and the product washed once with cold water. The flask and contents were dried *in vacuo* over calcium chloride. Wt. 765 mg. (62% from aniline), m.p. 175–176°.

Ethyl 3-Indoleacetate (VIII) and 3-Indoleacetic Acid (IX)

The half-ester (above) was dissolved in 12 ml. of diethylene glycol and the solution treated with 1 ml. of quinoline. Red cuprous oxide² (5–10 mg.) was added and the flask immersed in a hot oil bath. The bath temperature was raised rapidly to 200°, with stirring, and maintained there until vigorous gas evolution ceased (15 minutes). The mixture was then cooled and poured into 150 ml. of cold, dilute hydrochloric acid. The resulting mixture was extracted with ether, evaporated to an oil, and the latter taken up in 25 ml. of 95% ethanol and saponified with potassium hydroxide following the method outlined for the hydrolysis of the diester above.

²Prepared, with suitable particle size, by the action of glucose on hot Fehling's solution. The bright-red precipitate was washed three times with water, once with acetone, and dried. It may be kept indefinitely without losing its usefulness.

The crude 3-indoleacetic acid was precipitated by acidification with phosphoric acid. It was isolated and sublimed at high vacuum. The yield was 350 mg. (40% from aniline), m.p. 169-170°.

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CORRECTIONS

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Page 281. The heading of paragraph 2 of Experimental should read: "2-(β -Diisopropylaminoethyl-mercapto)-2-imidazolium Chloride Hydrochloride".

The heading of paragraph 3 of Experimental should read: "2-(β -Diethylaminoethyl-mercapto)-2-imidazolium Chloride Hydrochloride".

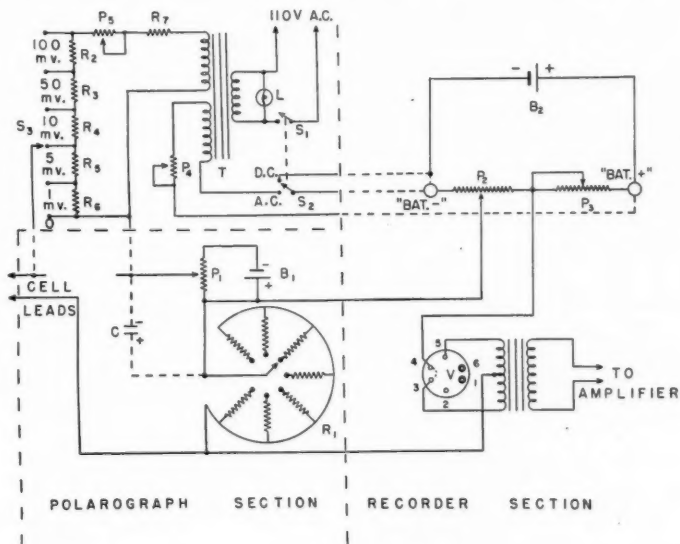
Page 454. On this page and in Table V the space group symbol for CoAs is erroneously given as *Pnma*. For the setting chosen this should read *Pmcn*.

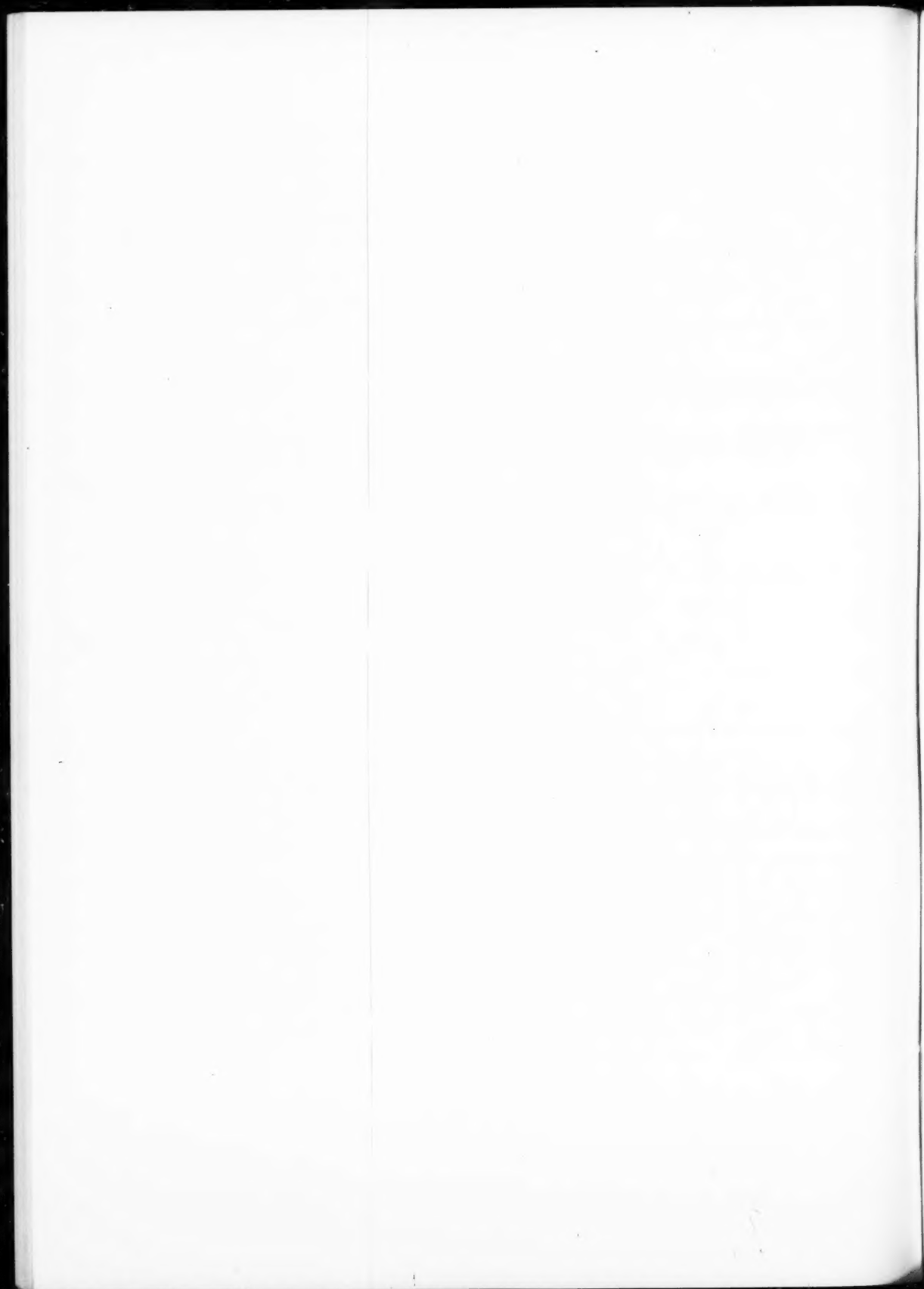
Page 915. The portion two inches down from the heading on the right side of Table I should read:

1802 ms	1794 } A	785 + 1030 = 1815 (A_1)
	1800 }	
	1807 }	
1858 ms	1851 } B	785 + 1081 = 1866 (B_1)
	1861 }	

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In the paper *A method of recording a-c. polarograms on a conventional d-c. polarograph* by D. M. Miller, pp. 942-947, Fig. 3 on p. 945 should be replaced by the figure appearing below.





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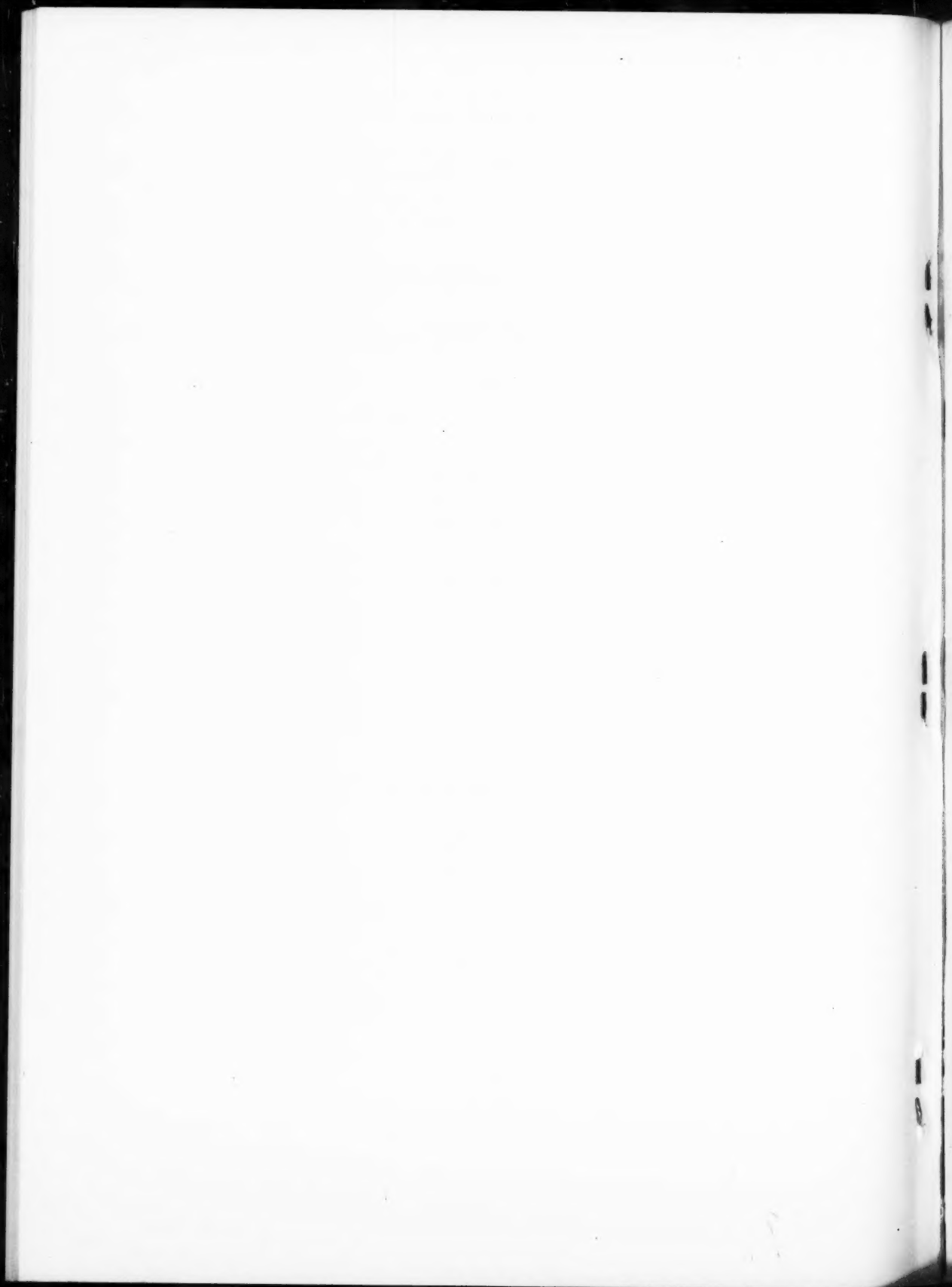
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